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COATED-PARTICLE FUEL DEVELOPMENT
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Metals and Ceramics Division

COATED-PARTICLE FUEL DEVELOPMENT AT OAK RIDGE NATIONAL LABORATORY

Compiled by

W. O. Harms

DATE ISSUED

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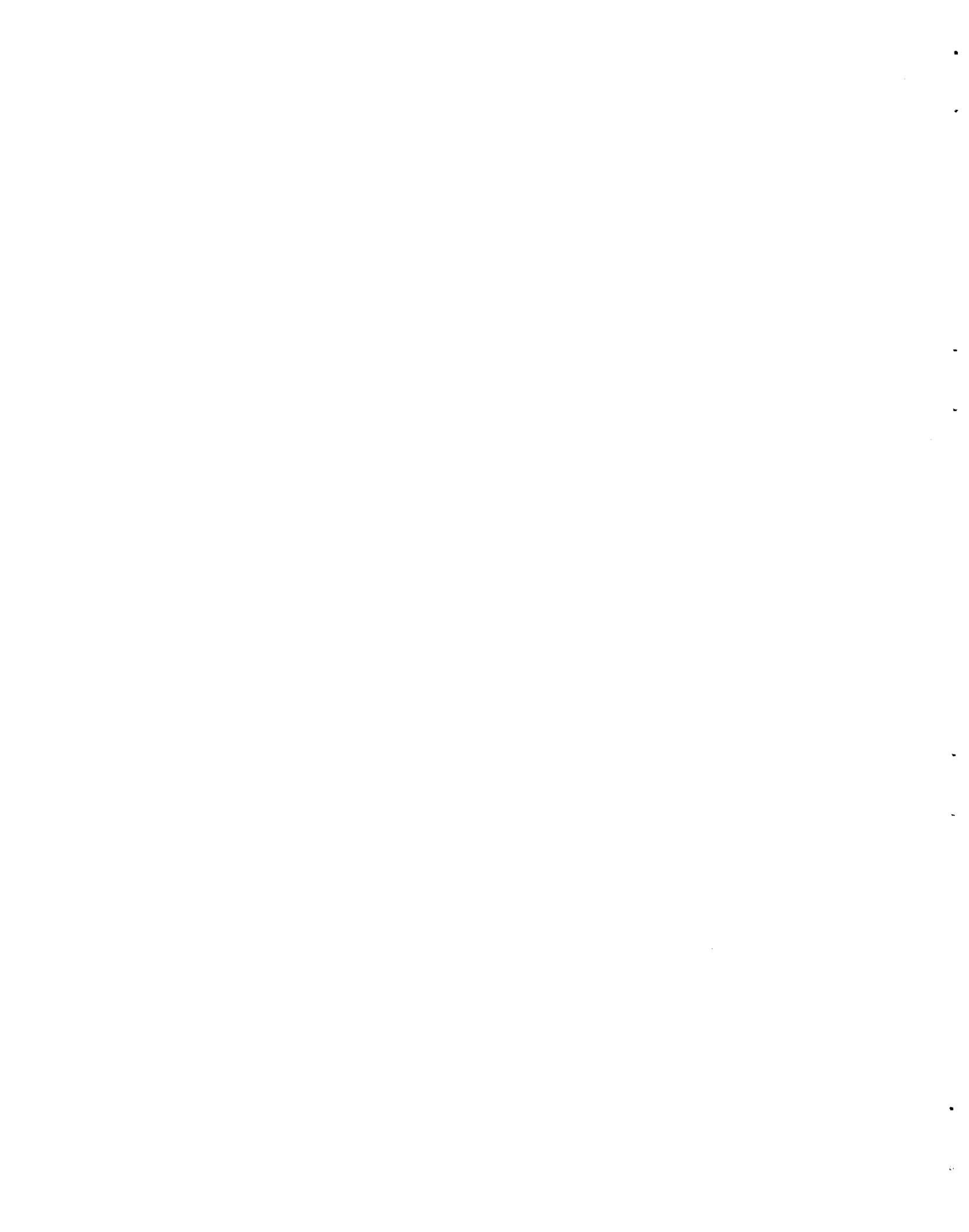


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ABSTRACT

The research program on coated-particle nuclear fuel materials at Oak Ridge National Laboratory has been concerned with three general problem areas: (1) A broad evaluation of materials involving pyrolytic-carbon-coated fuel carbides with major emphasis on the relationship between measurable properties and behavior during irradiation under simulated gas-cooled power reactor conditions; (2) studies on the compatibility of coated-particle materials with liquid coolants; and (3) chemical processing development for graphite-matrix fuels containing coated particles.

The techniques used and the significant results and implications that have evolved in this program are described.

INTRODUCTION

The research program on coated-particle nuclear fuel elements at the Oak Ridge National Laboratory (ORNL) has been concerned in large measure with the broad evaluation of materials for gas-cooled, fueled-graphite systems involving pyrolytic-carbon-coated carbide fuel particles. The major emphasis in this connection has been on investigation of the behavior of these materials under simulated power reactor conditions, particularly with regard to fission-product retention. The test conditions have included high burnups, partially oxidizing environments, and a wide range of temperatures. The results of these investigations, in conjunction with those from more specialized supporting studies, have served to elucidate those properties and phenomena governing the performance of the materials under consideration. In addition, they have served to delineate those problem areas requiring further research effort for exploitation of this coated-particle concept.

A less extensive part of the program at ORNL has consisted of determining the potential of coated-particle fuel materials, involving both oxide- and pyrolytic-carbon-coated particles, in a variety of liquid coolants. Compatibility studies have been carried out in pressurized water, organic-moderator coolants, and molten fluoride salts, and the effects of gamma irradiation have been investigated.

Methods for chemical processing of graphite-matrix fuels containing both carbon- and alumina-coated particles have been investigated on a laboratory scale. The methods include "grind-leach," combustion-dissolution, the hot 90% nitric acid process, anodic disintegration, and chloride volatility.

This paper describes the techniques used and the significant results and implications that have evolved in the three general problem areas comprising the ORNL Coated-Particle Fuel Element Development Program.

FUELED GRAPHITE, GAS-COOLED REACTOR APPLICATIONS

(F. L. Carlsen, Jr., Metals and Ceramics Division)

EVALUATION AND IRRADIATION TESTING

The evaluation and irradiation testing program has been concerned primarily with vendor-supplied coated-particle materials. Materials have been supplied by the Minnesota Mining and Manufacturing Company (3M), National Carbon Company (NCC), High Temperature Materials, Incorporated (HTM), General Atomic (GA), Nuclear Materials and Equipment Company (NUMEC), and Speer Carbon Company (SCC).

This portion of the program is conveniently divided into two sections: (1) tests on unsupported pyrolytic-carbon-coated carbide particles; and (2) tests on graphite-matrix elements containing coated particles. Detailed descriptions and results of the evaluation and irradiation tests have appeared in ORNL Gas-Cooled Reactor Program Progress Reports.¹⁻⁶

Unsupported Coated Particles

Unsupported coated particles have been studied in considerable detail and some 50 different batches have been examined. The fuel particles have for the most part been uranium carbide, although recently uranium-thorium carbide particles have been included.

¹GCR Quar. Prog. Rep. Mar. 31, 1961, ORNL-3102, pp. 104-7.

²GCR Quar. Prog. Rep. June 30, 1961, ORNL-3166, pp. 84-8.

³GCR Quar. Prog. Rep. Sept. 30, 1961, ORNL-3210, pp. 133-46.

⁴GCR Quar. Prog. Rep. Dec. 31, 1961, ORNL-3254, pp. 137-65.

⁵GCR Quar. Prog. Rep. Mar. 31, 1962, ORNL-3302, pp. 165-222.

⁶GCRP Semiann. Sept. 30, 1962, ORNL-3372 (in press).

Preirradiation Evaluation (E. S. Bomar, J. L. Cook, R. J. Gray,
R. W. McClung, Metals and Ceramics Division)

Unsupported coated particles are subjected to rigorous evaluation testing prior to in-reactor testing. The evaluation includes determination of the structure, shape, and dimensions of the coatings and particles, the amount of exposed fuel, the impurity content, the density, the crushing strength, and the effects of heat treatments.

Structure, Shape, and Dimensions. The structure of coated particles is determined by metallography, microradiography, and x-ray diffraction analysis. Photomicrographs showing the three principal types of pyrolytic-carbon coatings studied are shown in Figs. 1-3. The coating microstructure shown in Fig. 1 is termed laminar, because of its layer-like appearance. The structure shown in Fig. 2 is distinguished by its large, radially oriented grains and is described as columnar. Figure 3 shows the structure described as duplex because of the inner laminar coating, adjacent to the fuel particle, and the outer, fine-grained columnar coating. The uranium carbide particles generally are composed of UC_2 , as the major phase, with minor amounts of UC and graphite flakes.⁷ Generally there is a more or less continuous layer of graphite, which is present on the particles prior to coating, at the interface between the uranium carbide particle and the pyrolytic-carbon coating. Similar descriptions apply to uranium-thorium carbide particles.

X-ray diffraction analyses have been performed to determine the interlayer spacing and crystallite size of several coatings. The observed interlayer spacings range from 3.42 A to values greater than that for "turbostratic" carbon. (The interlayer spacing is thought to reflect the degree of stacking order in the graphite crystal structure. For ideal crystalline graphite this spacing is 3.354 A and for the completely disordered "turbostratic" carbon it is 3.440 A.⁸) The crystallite sizes of the coatings, as determined by x-ray diffraction

⁷C. K. H. DuBose and R. J. Gray, Metallography of Pyrolytic Carbon Coated and Uncoated Uranium Carbide Spheres, ORNL-TM-91 (Mar. 21, 1962).

⁸J. Bischoe and B. E. Warren, J. Appl. Phys. 13, 364 (1942).

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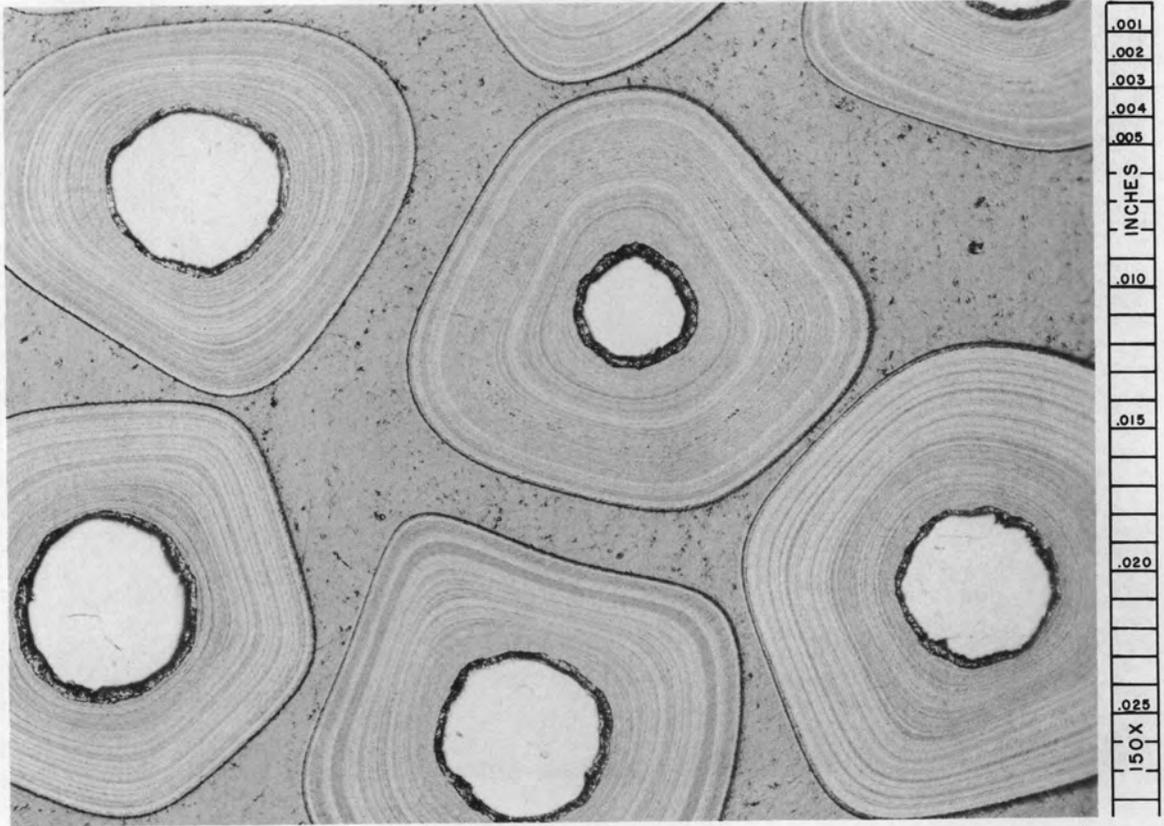


Fig. 1. Photomicrograph of Laminar-Pyrolytic-Carbon-Coated Uranium Carbide Particles from Batch 3M-SP-2. Bright-field. As-polished.

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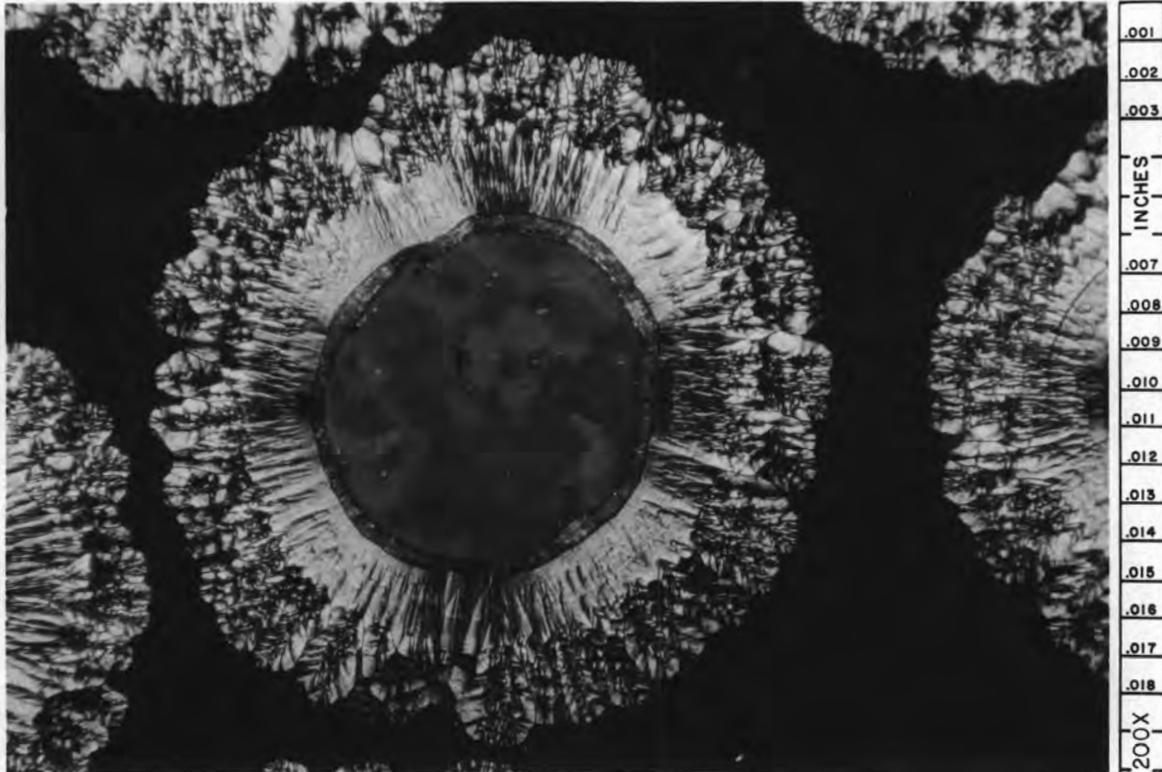


Fig. 2. Photomicrograph of Columnar-Pyrolytic-Carbon-Coated Uranium Carbide Particles from Batch HTM-1. Polarized light. Etchant: HAC, HNO₃, H₂O, 1:1:1.

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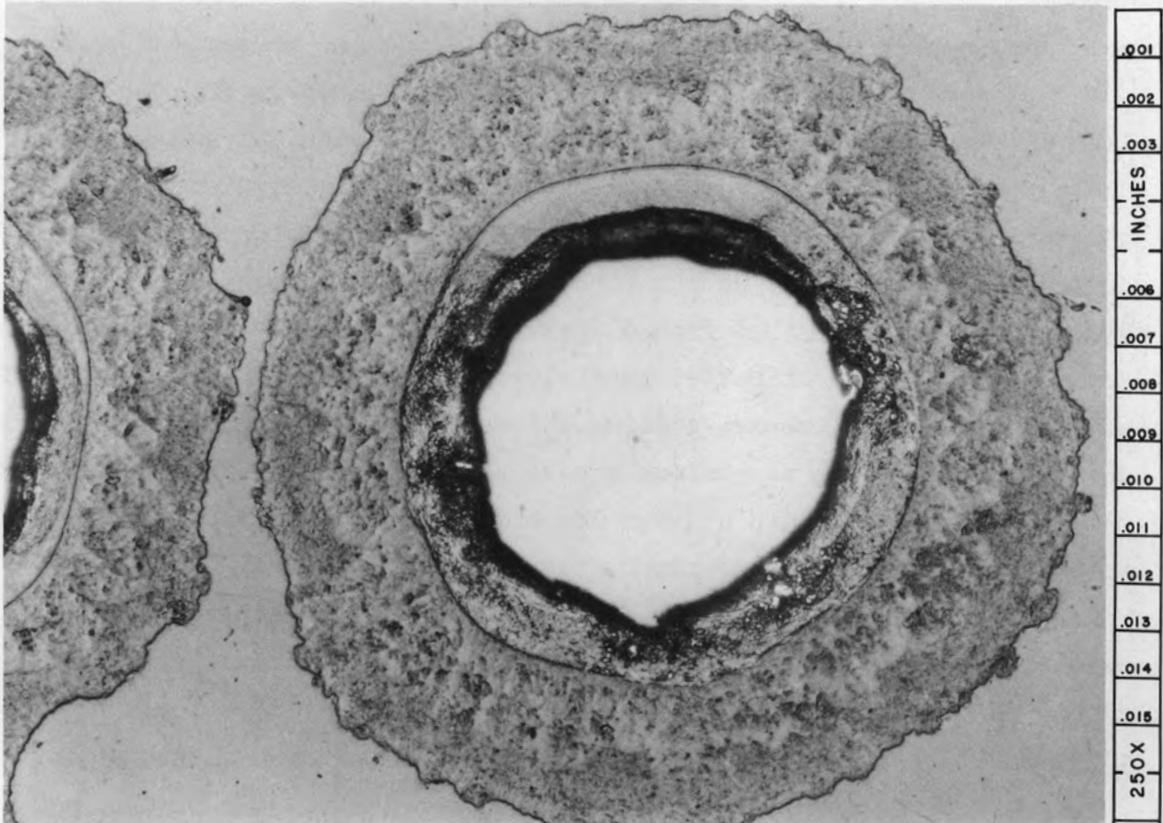


Fig. 3. Photomicrograph of Duplex-Pyrolytic-Carbon-Coated Uranium Carbide Particles from Batch NCC-AD. Bright-field. As-polished.

line broadening, range from 25 to 70 A for laminar coatings to 85 to 95 A for duplex coatings. In general, neither the c-spacing nor crystallite size correlate well with the type of coating microstructure.

Microradiographic examination gives additional information about the structure of coated particles.^{5,9} It is particularly useful in determining the extent of uranium migration in the pyrolytic carbon coatings (see, for example, Figs. 4 and 11) and the presence of void space between the coating and particle. This nondestructive technique also allows the accurate determination of the dimensions and shape of coated particles. Coating thickness is very accurately determined by this technique because the coating thickness at the midplane of a coated particle is very well defined in the microradiographs. The dimensions are determined from 50-particle samples selected at random. For a typical batch of coated particles, with an average particle diameter of approx 200 μ and average coating thickness of approx 100 μ , the standard deviations for these dimensions are 25 and 13 μ , respectively. The shape of the fuel particles in a given lot often ranges from nearly spherical to irregular with major-to-minor diameter ratios of 3:1.

Exposed Fuel. The amount of exposed fuel in a sample of coated particles is determined from measurements of the alpha activity and the amount of uranium removed by leaching in 8 M HNO₃ at 95°C for 8 hr. The alpha activity is proportional to the amount of uranium within approx 20 μ of the surfaces of the coated particles. The uranium removed by leaching comes both from particles with cracked coatings as well as from the surface of the coatings on sound particles. In general, the amount of exposed fuel is less than $5 \times 10^{-3}\%$ of that contained in the coated particles.

Impurity Content. Chemical analyses are used to determine the amount of uranium in the coated particles as well as the impurity content. The nature and quantity of the analytical data obtained, however, are such that no positive statement regarding impurity levels can be made at the present time.

⁹R. W. McClung, Techniques for Low-Voltage Radiography, ORNL-3252 (Feb. 14, 1962).

Density. Several methods have been evaluated for determining the density of both uncoated and coated particles. A technique employing a helium pycnometer is felt to be the most satisfactory.¹⁰ The density of the uncoated uranium carbide particles is generally between 10.0 and 11.0 g/cm³. The density of the coated particles depends upon the ratio of coating thickness to particle diameter and ranges between 2.5 and 6.5 g/cm³.

The density of the coatings is determined by a sink-float method on fragments obtained by crushing the coated particles with impact loading, followed by leaching in HNO₃ to remove the uranium carbide. By this method a range of density values is obtained for coatings in a given lot. For example, the densities of 89% of the fragments from a sample of duplex coatings were found to be in the range 1.86 to 1.92 g/cm³ and those for the remaining fragments were equally distributed above and below this range. The density of the laminar coatings examined has ranged between 1.95 and 2.01 g/cm³. The density of large-grained columnar coatings has not been determined.

Crushing Strength. Crushing-strength tests are performed by crushing individual coated particles from a randomly selected sample of 50 particles from each batch.⁶ For a typical batch of coated particles with an average crushing load of approx 1500 g, the standard deviations range from 200 to 300 g. The load at failure has been found to increase as the coating thickness increases; it is less dependent upon the structure of the coating.

Effects of Heat Treatments. The routine evaluation of a lot of coated particles includes a thermal-cycling test in which a sample from a given lot of particles, previously leached in 8 M HNO₃, is subjected to three thermal cycles between approx 200 and 1500°C with a one-hour exposure at the temperature extremes in each cycle. The sample is heated in a small induction furnace which allows very rapid heating and cooling. The effect of the thermal cycling is determined by measuring the amount of exposed uranium by the acid-leaching and alpha-counting techniques. In general, the alpha activity is slightly increased

¹⁰P. Hidnert, Density of Solids and Liquids, NBS Circular 487, p. 24 (Mar. 15, 1950).

and the exposure to nitric acid results in the removal of quantities of uranium equal to or slightly greater than that for the as-received particles.

Extended heat treatments are employed to determine the long-time stability of coated particles, particularly with regard to uranium migration. In some tests the thermal conditions are selected to match those experienced by samples in irradiation experiments. In tests of several hundred hours it has been demonstrated that some uranium migration can occur⁶ at temperatures up to 1400°C; however, complete penetration of 100 μ -thick coatings has not been observed under these conditions. Heat treatments at higher temperatures result in an acceleration of the uranium migration. At 1900°C, for example, uranium migration is observed in only five minutes; complete penetration at 1900°C, however, requires exposure times greater than 100 hr.

The effect of heat-treatment temperature on uranium migration in lamina-coated particles is shown in the microradiographs of Fig. 4. Figure 4a shows the as-received material (no uranium apparent in the coatings). Figure 4b was taken after a heat treatment at 1750°C for 3 hr and shows that substantial uranium migration occurred. Figure 4c indicates that the effect of heat treatment for 5 min at 1950°C is similar to that after 3 hr at 1750°C.

Irradiation Tests (R. R. Sellers, Reactor Division; P. E. Reagan, R. M. Carroll, D. F. Toner, Reactor Chemistry Division; J. L. Scott, E. L. Long, Metals and Ceramics Division)

Neutron-Activation Tests. The irradiation testing of coated-particle materials begins with neutron-activation tests. These tests involve short-time exposures of samples at low temperatures in the ORNL Graphite Reactor followed by out-of-reactor heat treatments during which the fission-product release behavior is determined.¹¹ Irradiation times and fluxes are selected to give about 10^{15} fissions per sample. The resulting sensitivity for the detection of Xe^{133} is approx $3 \times 10^{-5}\%$ of the Xe^{133} present. For screening-type tests designed to evaluate coating integrity, the postirradiation heat treatments are conducted at 1400°C for approx 3 hr. Other heat treatment conditions are used in studies

¹¹GCR Quar. Prog. Rep. Dec. 31, 1959, ORNL-2888, p. 68.

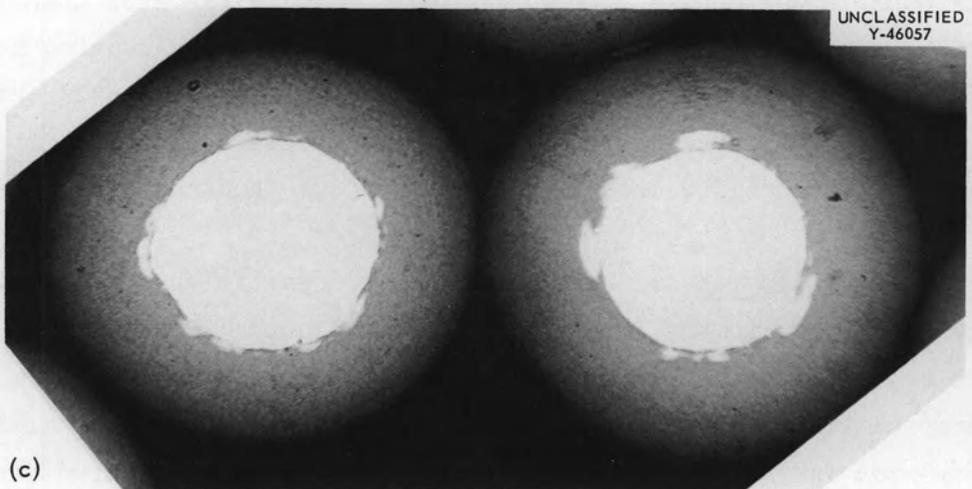
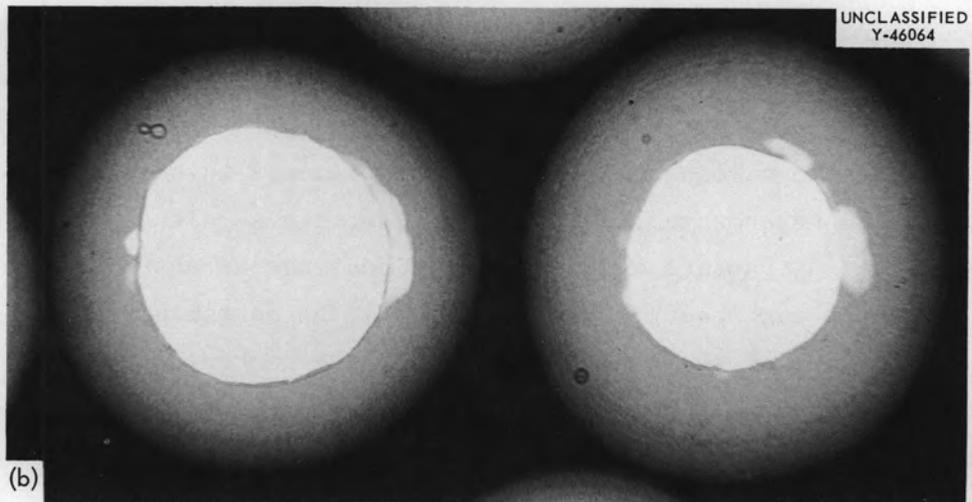
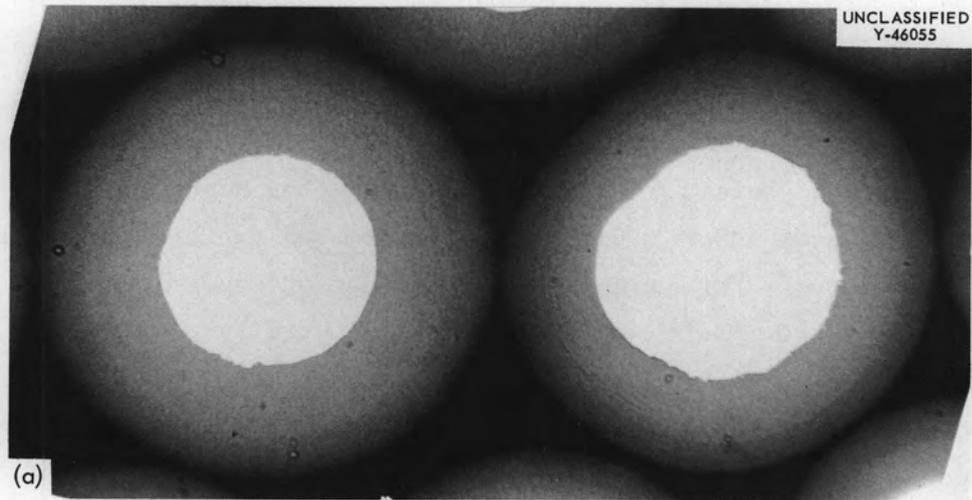


Fig. 4. Microradiographs of As-Received and of Heat-Treated Samples of Laminar-Pyrolytic-Carbon-Coated Particles from Batch 3M-102-B. a. As-received; b. heat treated at 1750°C for 3 hr; c. heat treated at 1950°C for 5 min. 200X. Reduced 16%.

designed to provide data on the mechanism of fission-product release and to establish the ultimate limitations of coated-particle fuels.

The neutron-activation experiments have shown that for coated particles having low amounts of exposed fuel ($< 10^{-2}\%$), less than $2 \times 10^{-4}\%$ of the contained Xe^{133} is released after heating for 3 hr at 1400°C . The large majority of the samples tested exhibit these very low release rates. For samples having amounts of exposed uranium exceeding 0.1% the fission-gas release is essentially proportional to the amount of exposed uranium. For samples with less than about 0.1% of exposed uranium, the detectable fission-gas release seems to be independent of the amount of exposed uranium.

Neutron-activated coated-particle samples have been heat treated to temperatures much higher than 1400°C with very interesting results. Thermal treatments at 1960°C for 140 hr did not cause increased fission-gas release for uranium carbide particles with approx 100μ -thick laminar pyrolytic-carbon coatings. Heat treatments to temperatures of 2050°C for 103 hr, however, resulted in fission-gas-release bursts characteristic of rupture of the particle coatings as shown in Fig. 5. The first burst was observed after 37 hr and the second after approx 42 hr; at the end of the 103-hr test period the number of recorded bursts indicated that approx 53 particles in the 100-particle sample had ruptured. Subsequent examination of the particles revealed that coatings on this number of particles had indeed ruptured.

In other experiments², where the Xe^{133} release was less than $3 \times 10^{-3}\%$, significant amounts of Ba^{140} were detected on heating at temperatures between 1400 and 1900°C . Release of iodine, tellurium, and silver has been observed at temperatures as low as 1000°C . At 1000°C the fractional release of silver was four thousand times that of Xe^{133} .

Static Capsule Tests. Unsupported coated particles are irradiated in static capsules in the Low Intensity Test Reactor (LITR). Each capsule consists of two containers, of the type shown in Fig. 6, which are encapsulated in an atmosphere of helium and hermetically sealed in a compartmented Inconel tube. Tantalum-sheathed tungsten-rhenium thermocouples are used to measure the central temperature in each container.

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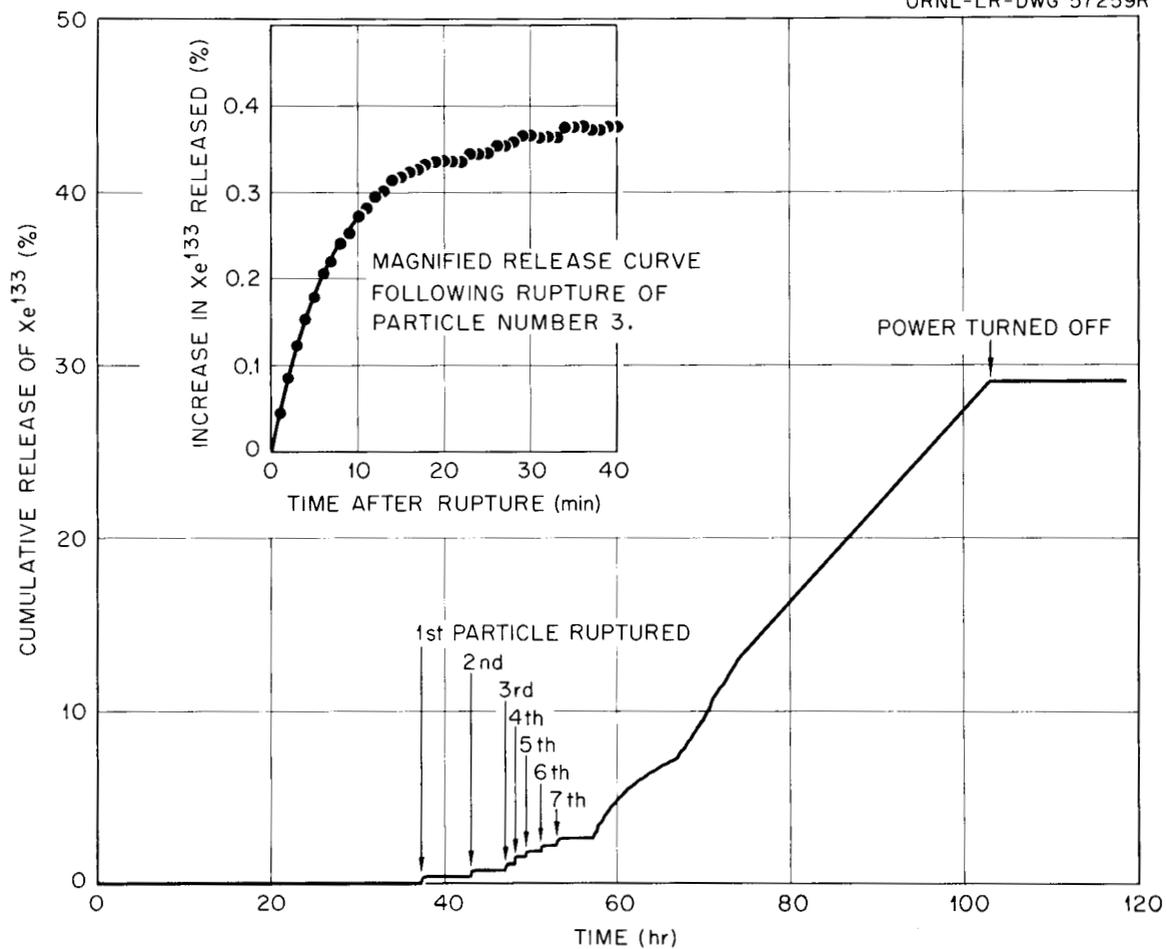


Fig. 5. Release of Xe^{133} from Irradiated Pyrolytic-Carbon-Coated Uranium Carbide Particles During Heating at $2050^{\circ}C$ After Neutron Activation.

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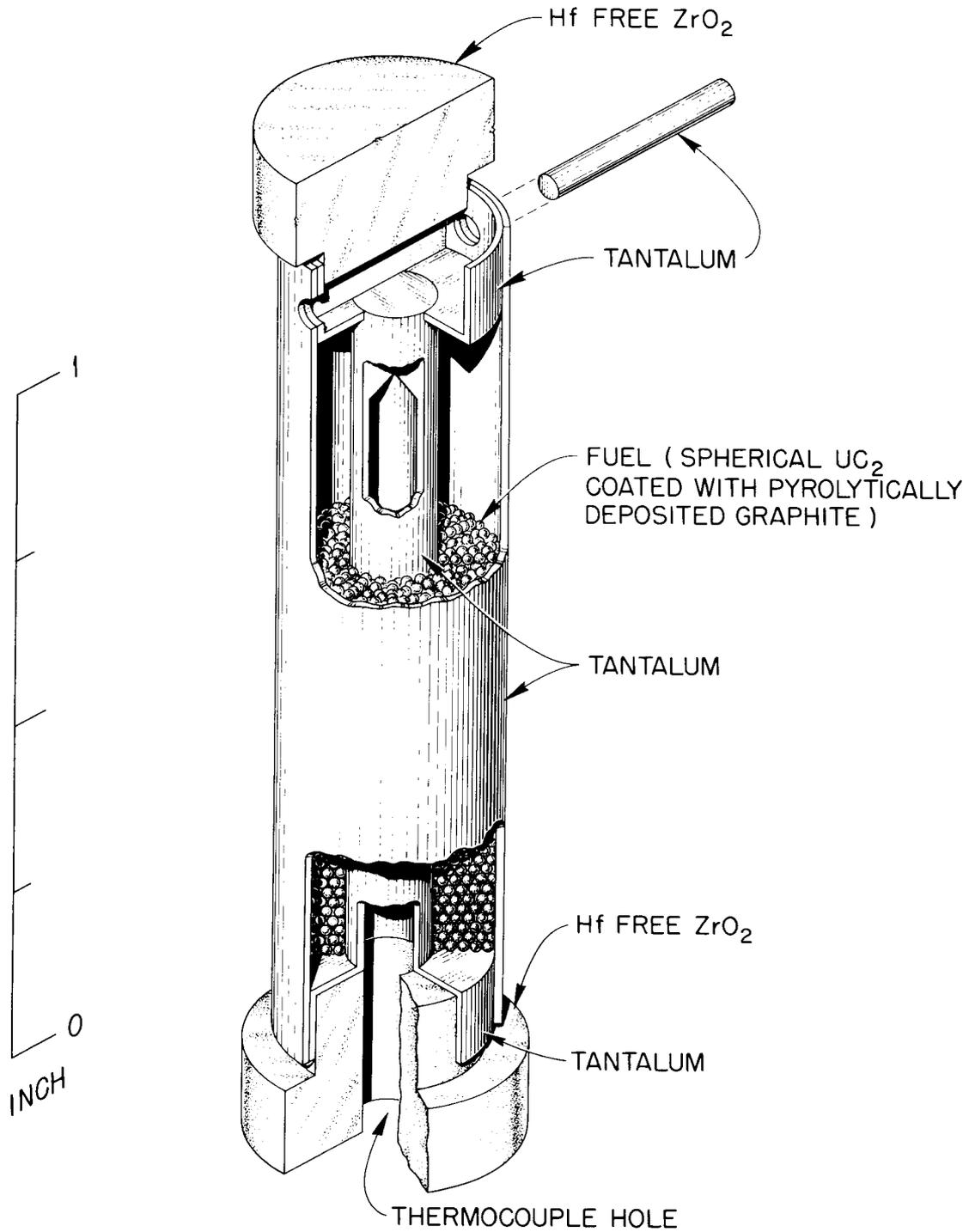


Fig. 6. Container Used in Static Capsule Tests of Coated Particles in the LITR.

The results of four static capsule tests that have been completed are summarized in Table 1.²⁻⁶ The purpose of these tests was to assess the role of coating microstructure and of coating thickness on the irradiation stability of the coated particles at 2000 to 2500°F after burnups of 5 to 6 at. % of total uranium. Cracked coatings were found in all of the samples, and the fraction that was cracked depended upon the microstructure and thickness of the coatings. The 100 μ -thick coatings with the duplex microstructure were the most stable under the irradiation conditions employed, whereas, the columnar coatings that were only 50 μ in thickness were badly damaged.

A photograph of the laminar-coated particles showing cracked coatings after irradiation is presented in Fig. 7. A cross section of a particle with a cracked laminar coating is shown in Fig. 8 and is to be compared with that of duplex-coated particles in Fig. 9. The superior performance of the duplex coatings may be associated with the presence of the discontinuity that exists between the laminar and columnar portions of the coating and to the fact that fission recoil damage, at least initially, is confined to the inner layer.

Several additional observations of interest have been made in connection with these experiments. The first is that dumbbell-shaped coated particles (doublets) crack more readily than the spherical particles. In the postirradiation examination of the 100 μ -thick columnar-coated particles irradiated in the LCP-1 experiment, it was noted that the majority of the cracked-coated particles were doublets, as shown in Fig. 10. Secondly, the effect of an impure environment was noted when air leaked into the LCP-1a and LCP-2a compartments. As noted in Table 1, the number of cracked coatings and the amount of exposed uranium for particles in the compartments containing air were several times greater than that in the compartments containing pure helium.

The extent of uranium migration that occurred in the laminar-coated particles under the irradiation conditions of the LCP-2b experiment was determined by microradiography. As shown in Fig. 11, the uranium migrated to a depth of approx 25 μ or approx 1/4 of the coating thickness.

Table 1.. Results of Static Capsule Irradiation Experiments
on Unsupported Pyrolytic-Carbon-Coated Uranium Carbide Particles

Experiment Number	Coating Structure	Average Coating Thickness (μ)	Approximate Temperature ($^{\circ}$ F)	Approximate Burnup (at. % of Total U)	Cracked Coatings ^a (%)	Exposed Uranium ^b (%)	Kr ⁸⁵ Release ^c (%)
LCP-2a	Laminar	100	2350	6	17 ^d	10 ^d	d
LCP-2b	Laminar	100	2500	6	2-4	0.6	0.4
LCP-1a	Columnar	100	1950	5	3 ^d	20 ^d	d
LCP-1b	Columnar	100	2100	5	1-2	2	0.2
LCP-4a	Columnar	50	2500	6	52	96	e
LCP-4b	Columnar	50	2500	6	45	48	e
LCP-3a	Duplex	100	1950	5	0.3	0.04	e
LCP-3b	Duplex	100	2100	5	0.3	0.18	e

^aDetermined by visual examination at approx 30X, and by metallographic examinations at higher magnifications.

^bDetermined by leaching in 8 M HNO₃ at 95 $^{\circ}$ C for 8 hr; expressed as per cent of total uranium.

^cBased on analysis of gas released on puncturing the container.

^dCompartment failed with subsequent air inleakage.

^eNot determined.

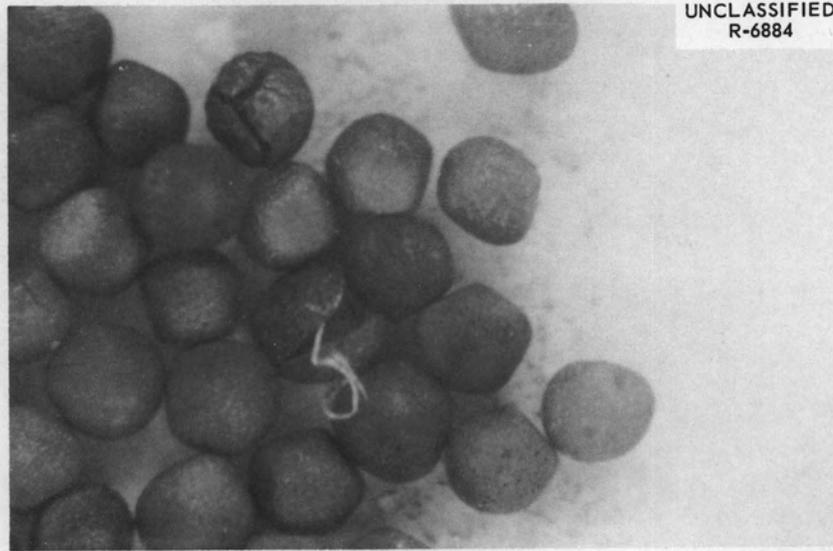


Fig. 7. Photograph of Pyrolytic-Carbon-Coated Uranium Carbide Particles from Batch 3M-SP-2 After Irradiation in Static Capsule LCP-2a at Approximately 2350°F to a Burnup of Approximately 6 at. % of the Total Uranium. Unmounted, oblique lighting. 60X.

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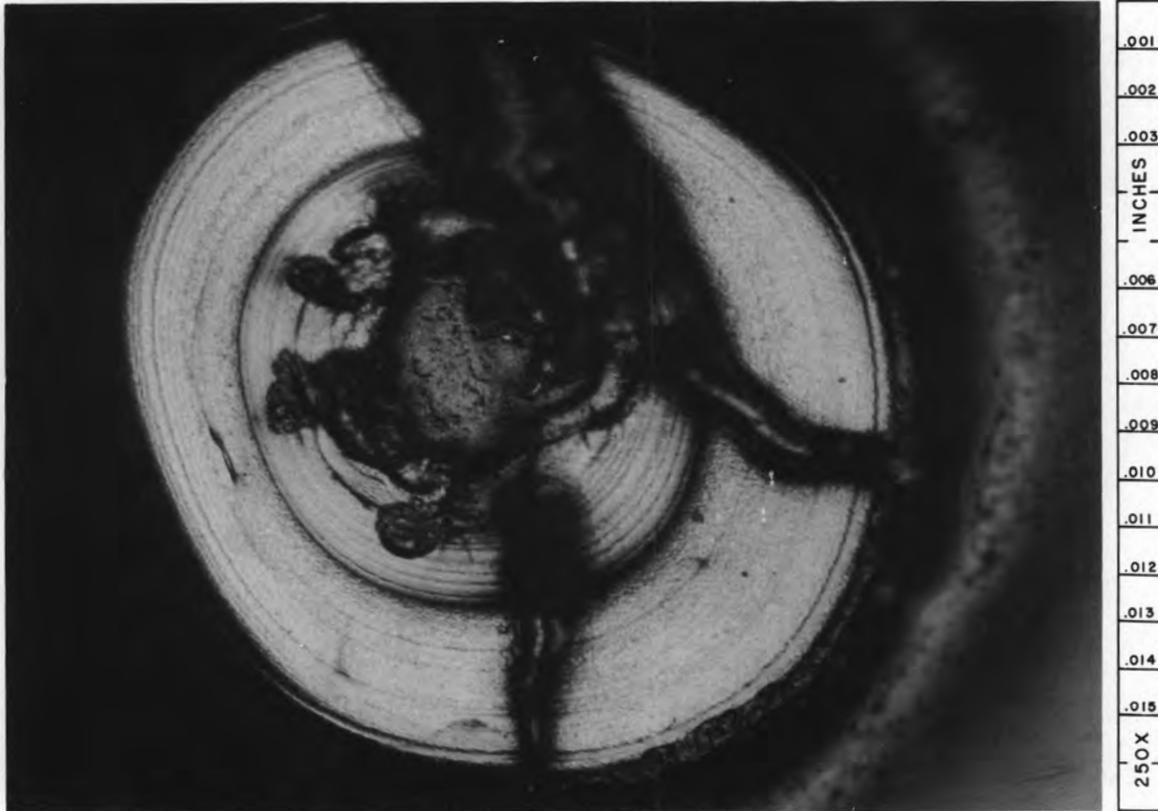


Fig. 8. Photomicrograph of a Cracked Laminar-Coated Particle from Batch 3M-SP-2 After Irradiation in Static Capsule LCP-2b at Approximately 2500°F to a Burnup of Approximately 6 at. % of the Total Uranium. Bright-field. Etchant: HAC, HNO₃, H₂O, 1:1:1. 250X.

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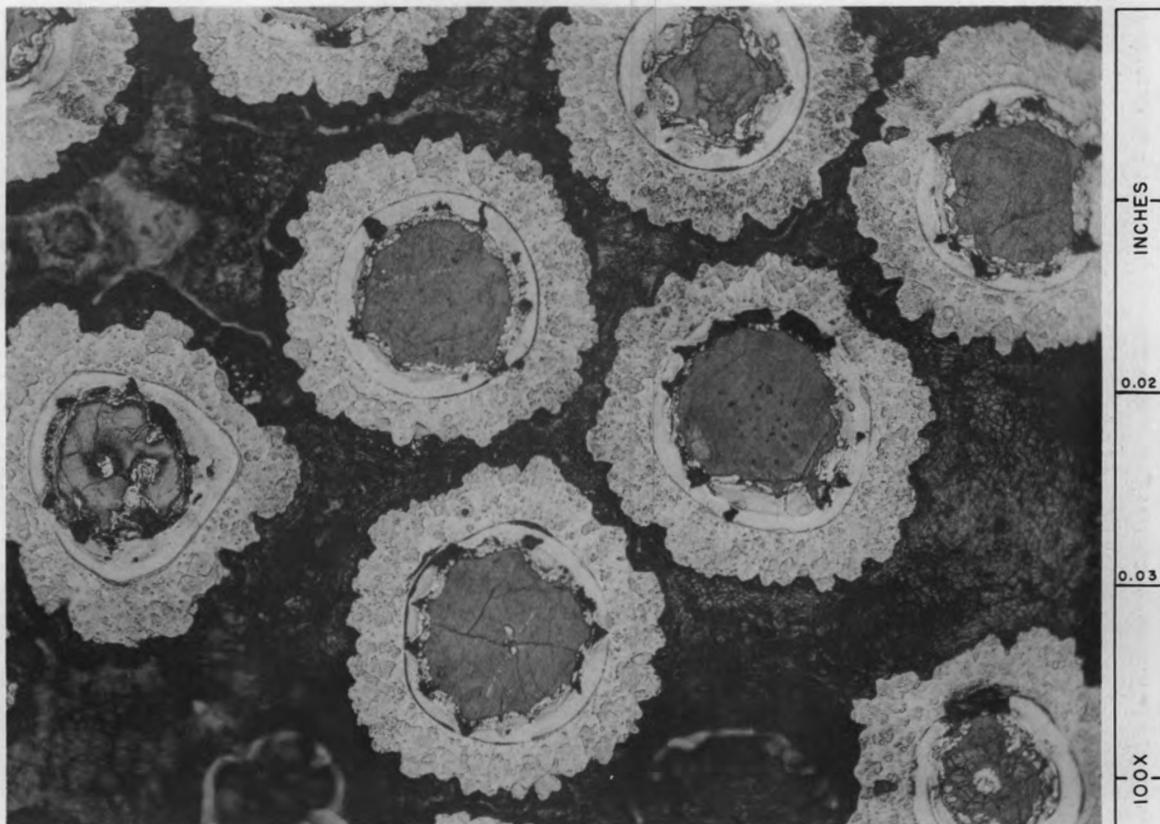
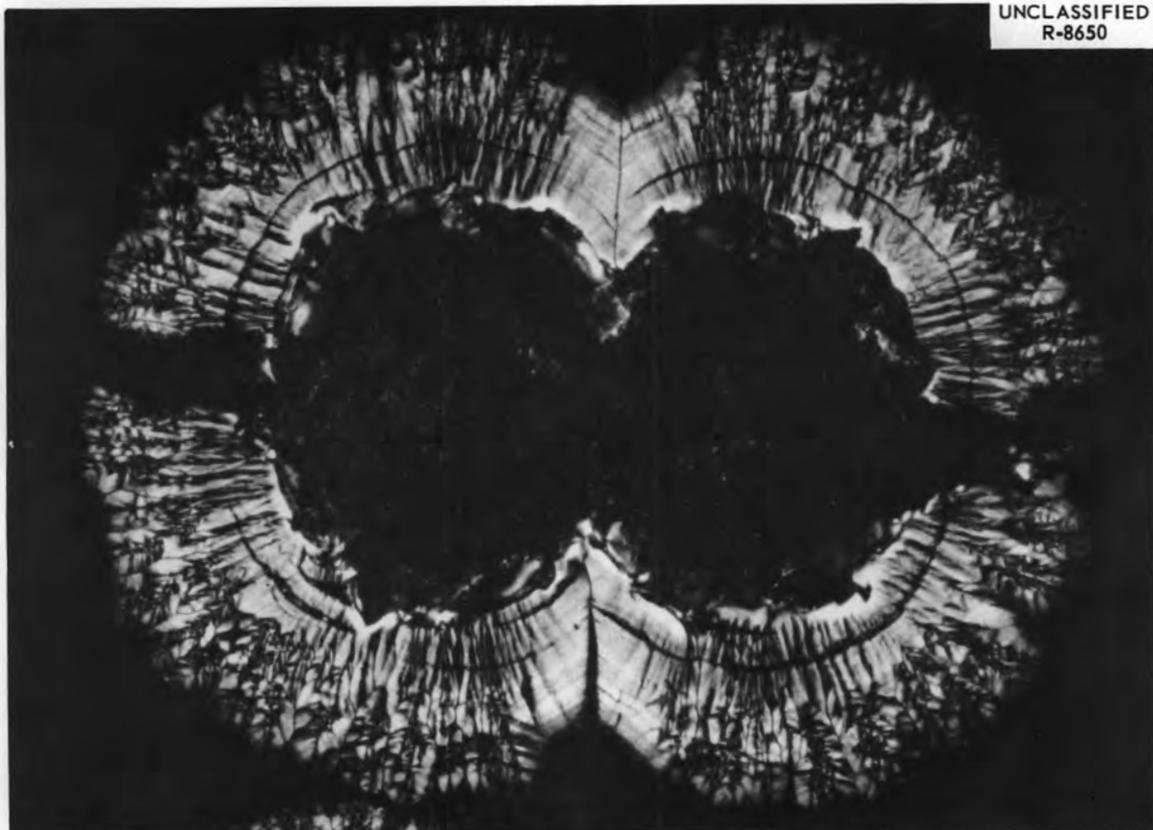
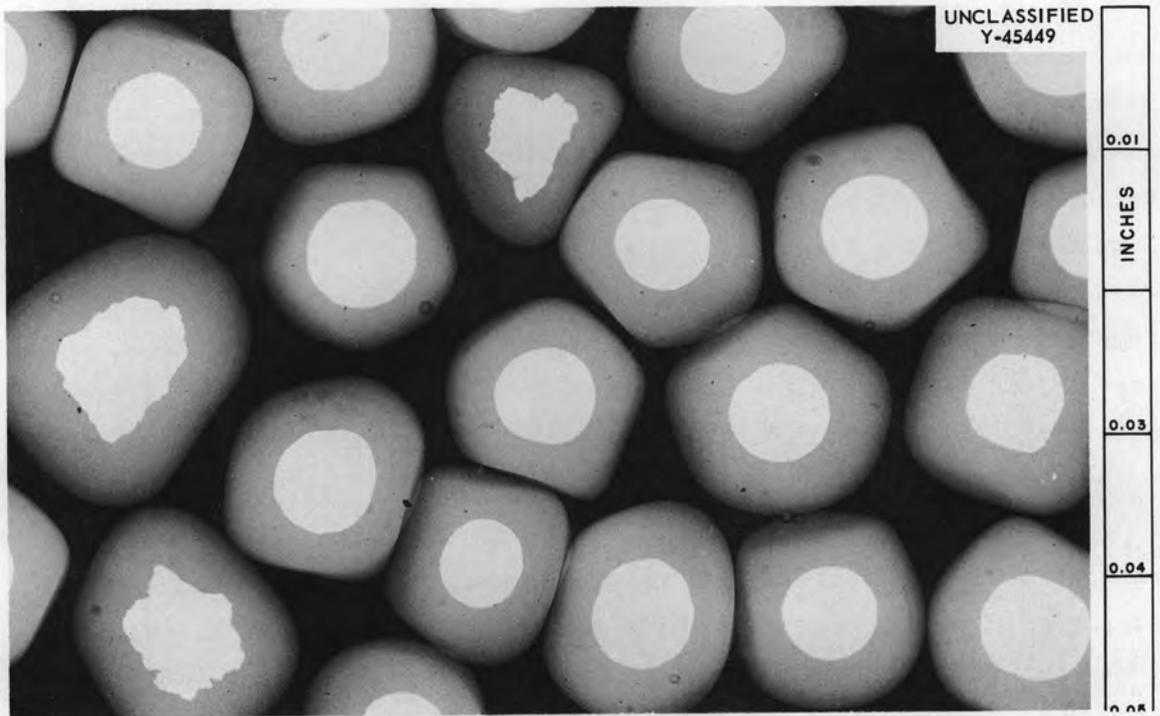


Fig. 9. Photomicrograph of Duplex-Coated Particles from Batch NCC-BE After Irradiation in Static Capsule LCP-3 at 2100°F to a Burnup of Approximately 5 at. % of the Total Uranium. Bright-field. Etchant: HAC, HNO₃, H₂O, 1:1:1.

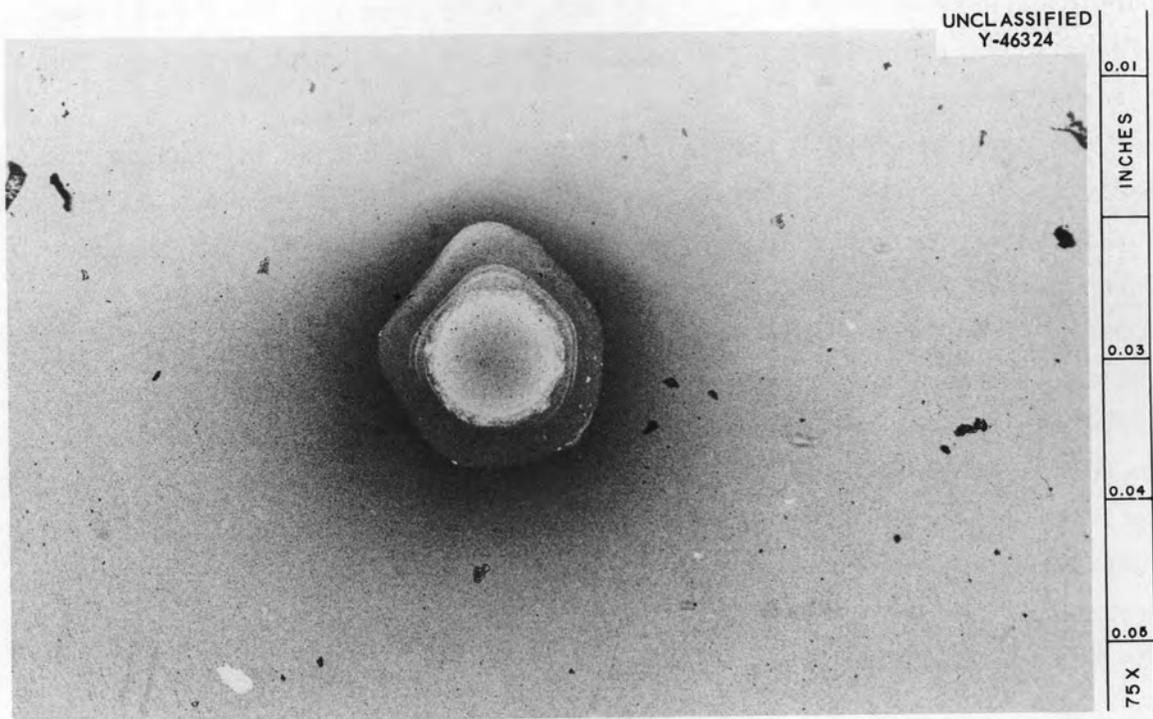


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Fig. 10. Photomicrograph of a Columnar-Coated Particle from Batch HTM-1, Irradiated in Capsule LCP-1b at 2100°F to a Burnup of Approximately 5 at. % of Total Uranium. Bright-field. Etchant: HAC, HNO₃, H₂O, 1:1:1. 150X.



(a) As-received



(b) Irradiated

Fig. 11. Microradiograph of Laminar-Coated Particles from Batch 3M-SP-2. a. As-received; b. irradiated in Capsule LCP-2b at 2500°F to a burnup of approximately 6 at. %. 75X.

Sweep Capsule Tests. Sweep capsule irradiation experiments are performed on unsupported coated particles in the B9 and C1 core positions of the Oak Ridge Research Reactor (ORR).^{5,6} In these experiments, fuel assemblies of the type shown in Fig. 12 are continuously purged with helium and the gas stream is continuously monitored for gamma activity. Samples of the gas are withdrawn periodically for analysis of fission gases by gamma-ray spectrometry. The neutron flux and the operating temperature can be independently varied over wide ranges in these facilities. Neutron fluxes up to approx 1×10^{14} neutrons/cm².sec are obtainable and the flux can be determined at any time by introducing argon into the sweep gas and measuring the Ar⁴¹ activity.

Uranium carbide particles with each of the three types of pyrolytic-carbon coatings - that is, laminar, columnar, and duplex - and one sample of uncoated uranium carbide particles have been irradiated in these facilities. The average coating thickness was approx 100 μ and the fuel particle diameters ranged between 175 and 250 μ . The results are summarized in Table 2. Fission-gas-release rates from the duplex-coated particles were substantially lower than those from the other two types of coated particles tested, a result which is consistent with that for the static capsule tests.

In experiment B9-8, bursts of fission gas were observed during the early stages of the 1700°F exposure and the release rates were essentially constant for the remainder of the 13 at. % burnup at this temperature. This observation and the fact that during subsequent irradiation at 800 and at 600°F the release rates were higher than those during the initial exposure for 15 at. % at 1500°F indicate that cracking of coatings occurred as the result of the increase in temperature to 1700°F in this experiment. In all tests, primarily during the early stages, activity bursts were frequently observed and the gas samples withdrawn shortly after these bursts were found to contain inordinately large amounts of the long-lived Xe¹³³ isotope. These observations suggest that the bursts, which occurred more frequently from the laminar-coated particles than from the other two types, were caused by the rupturing of individual particle coatings.

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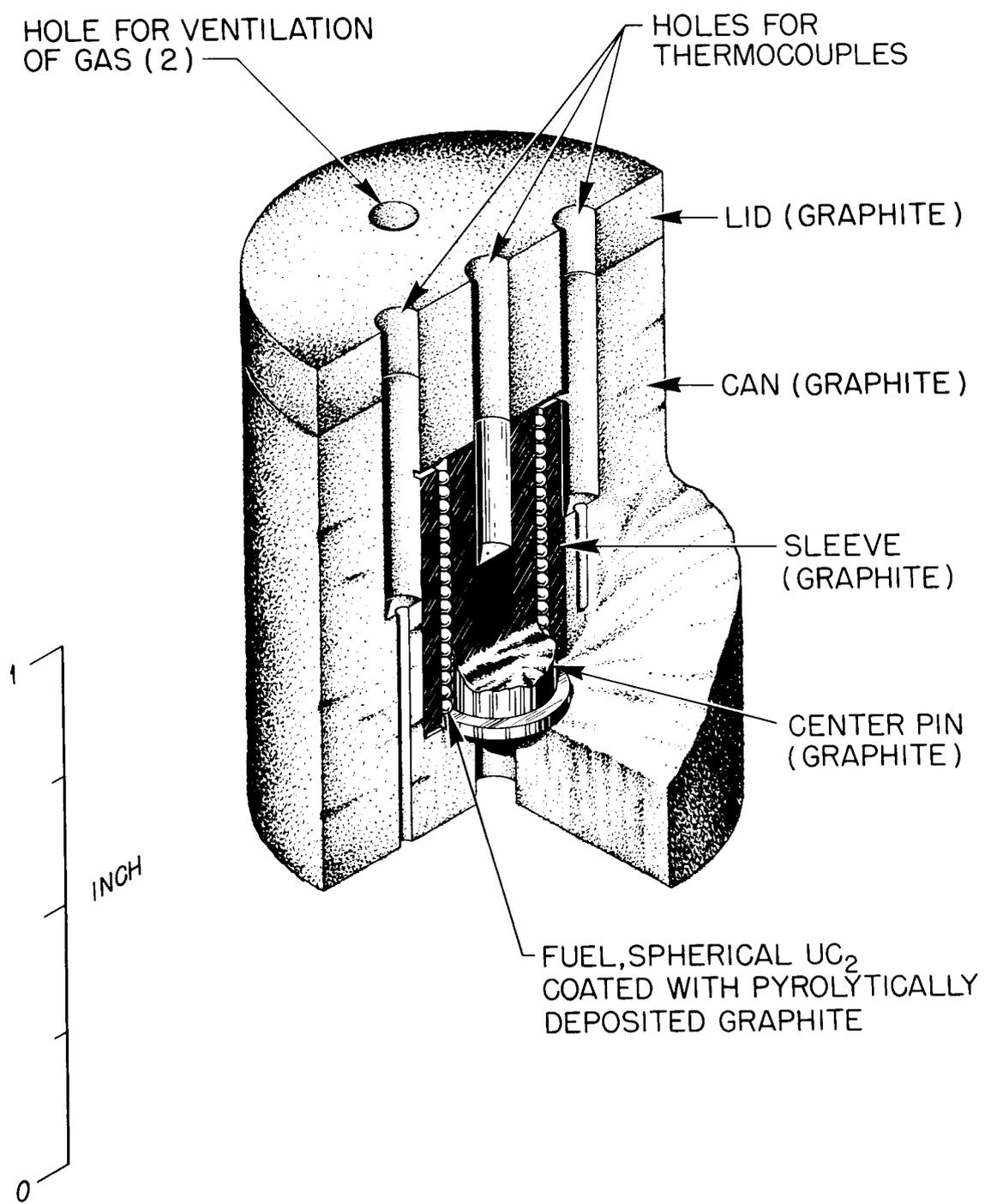


Fig. 12. Capsule for Irradiation of Coated Particles in the ORR-B9 and ORR-C1 Sweep Gas Facilities.

Table 2. Results of Sweep Gas Irradiation Experiments on Unsupported Pyrolytic-Carbon-Coated Uranium Carbide Particles

Experiment No.	Coating Structure	Approximate Temperature (°F)	Burnup Range (at. % of Total U)	R/B ^a for Kr ⁸⁸	Cracked Coatings (%)
				$\times 10^{-5}$	
C1-8	(Uncoated)	1500	0 - 4.3	530	b
C1-7	Laminar	1500	0 - 15	18	5
B9-7	Columnar	1500	0 - 8	2.7	2
		1650	8 - 12	10	
B9-8	Duplex	1500	0 - 14.7	0.4	< 0.5
		1700	14.7 - 27.8	2.1	
		800	27.8 - 28.9	1.0	
		600	28.9 - 29.7	0.9	
B9-9	Duplex	800	0 - 4	0.8	c

^aR/B is the average value at steady state of the ratio of the release rate to the birth rate.

^bNot applicable.

^cNot determined (experiment in progress).

The half-life dependence of the fission-gas-release rates at 1500°F is given in Fig. 13. The half-life dependency for release from columnar- and duplex-coated particles is about the same as that for the uncoated particles, indicating that the mechanism of release from cracked coatings in these tests was similar to that from uncoated particles. (The dashed line labeled "Selected PBRE Criterion" in Fig. 13 represents an improvement in performance by a factor of 50 relative to uncoated particles.)

Summary and Discussion

The results of these tests have demonstrated that a high level of performance with respect to fission-gas retention, and, therefore, irradiation stability, can be achieved in gas-cooled reactor fuels containing pyrolytic-carbon-coated carbide particles. Steady-state R/B values in the range 10^{-6} to 10^{-5} have been obtained at 1500-1700°F after burnups as high as 28 at. % of total uranium. The performance of the pyrolytic-carbon-coated particles studied depends primarily upon the structure and thickness of the coatings and to some extent on the shape of the carbide particles. The performance of coatings with the duplex structure has been superior to that of coatings with either the laminar or the columnar structures.

The curious fact that only a small percentage of the coatings with average thickness of approx 100 μ have failed during extended irradiations indicates that there are "weak sisters" which have passed the preirradiation evaluation tests. Microradiographic examinations have shown that coating thickness is quite variable within given batches of coated particles. A comparison of the coating-thickness data with irradiation test results indicates that there is a good correlation between minimum coating thickness for a population and either the fission-gas release or the percentage of coatings cracked during irradiation. A similar correlation exists between minimum crushing strength and irradiation performance. These correlations suggest that the "weak sisters" may simply be those coated particles with thin and, therefore, weak coatings. In this connection, it is in order to note that more than 50% of the coatings failed by cracking in a single test on particles with an average coating thickness of approx 50 μ .

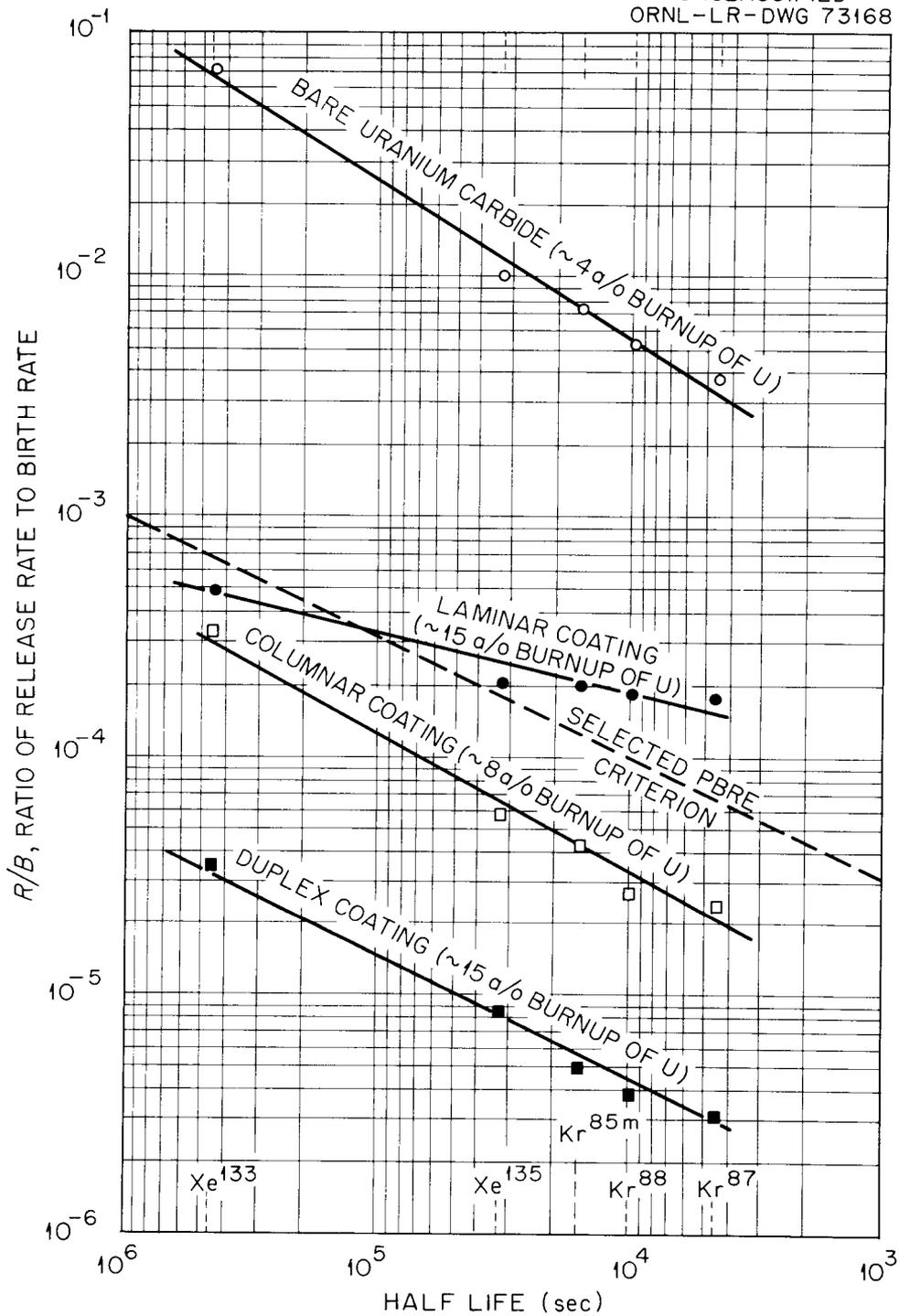


Fig. 13. Relationship Between R/B and Half-Life for Release of Inert Gases from Pyrolytic-Carbon-Coated and Uncoated Uranium Carbide Particles at 1500°F. (Calculation of R/B for Kr^{85m} is based on fission yield of 2.0%.)

Fueled Graphite Elements Containing Coated Particles

Preirradiation Evaluation (E. S. Bomar, R. W. McClung, R. J. Gray, Metals and Ceramics Division)

Graphite-matrix elements containing pyrolytic-carbon-coated particles and having geometries ranging from small, right-cylindrical pellets to 1 1/2-in. -diam spheres, both with and without unfueled shells, have been evaluated. The evaluation procedure includes visual and dimensional inspections, density determinations, determination of the distribution of coated particles, measurements of exposed fuel and fuel loading, structure determinations, and measurements of fracture strength.^{3,4,6}

Visual Examination and Dimensions. Visual examinations have shown that the surface condition of the graphite-matrix elements is quite variable. Cylindrical elements with unfueled shells generally are smooth, although sharp corners are often chipped. Coated particles, sometimes in aggregates of three to six particles, are frequently visible on or as slight protrusions from the surface of elements without unfueled shells. Spherical elements frequently exhibit die marks and seams or molding flashes.

Dimensional variations, defined as the difference between maximum and minimum dimensions of elements within a lot divided by the average for the lot, have ranged from 0.001 to 0.07, depending upon the shape and size of the elements. For 1 1/2-in. -diam spheres the dimensional variation has not exceeded 0.02. The thickness and quality of unfueled shells are determined by radiographic and metallographic examinations. The shells on cylindrical and bushing-shaped elements have been quite variable in thickness. In some places the shells are twice the nominal thickness and in others essentially no shell is apparent. The 1/4-in. -thick shells on spherical elements, on the other hand, have been very uniform in thickness. The shells appear to be well bonded to the fueled regions, with no apparent change in the microstructure of the graphite matrix at the interface.

Density. The bulk densities are determined from dimensional and weight measurements and have ranged from 1.54 to 2.10 g/cm³, depending upon the fuel loading and manufacturing techniques used by the vendors.

The average net carbon density is determined by analyzing several elements from a lot and subtracting the weight of uranium and thorium before calculating the density. Average net carbon densities have ranged from 1.44 g/cm³ to 1.93 g/cm³. With a few exceptions, all elements have exceeded the minimum bulk density of 1.70 g/cm³ and net carbon density of 1.65 g/cm³ as presently specified.

Distribution of Coated Particles. The uniformity of distribution of coated fuel particles within graphite-matrix fuel elements, as determined by radiographic and metallographic examinations, has been quite variable. The distribution in bushing-shaped elements has ranged from very uniform in some cases to very nonuniform in others. In extreme cases the fuel particles are concentrated near the inside surface, leaving low-density areas near the outside surface. Metallographic examinations have shown that, in general, the distributions in spherical elements are quite uniform. The uniformity of distribution is difficult to assess in radiographs of spherical elements.

Exposed Fuel and Fuel Loading. A measure of the exposed fuel is provided by alpha counting and by the amount of uranium removed by leaching in 8 M HNO₃. Exposed fuel in some of the graphite-matrix elements received early in the program corresponded to as much as 2% of the contained uranium; for elements received more recently, however, less than 0.05% exposed fuel has been detected. The total amount of fuel is determined by chemical analysis. The vendors' control of the fuel loading in a given element has been adequate (±5%).

Structure. Microstructures representative of bushing-shaped elements from three different vendors are shown in Figs. 14, 15, and 16. The obvious differences in these microstructures indicate that the manufacturing processes used in preparing the elements were significantly different. The quantity of binder residue (light-gray material) is greatest in the matrix shown in Fig. 16. The coated particles shown in Figs. 15 and 16 are apparently well bonded to the matrix, whereas, those in Fig. 14 are surrounded by small void regions.

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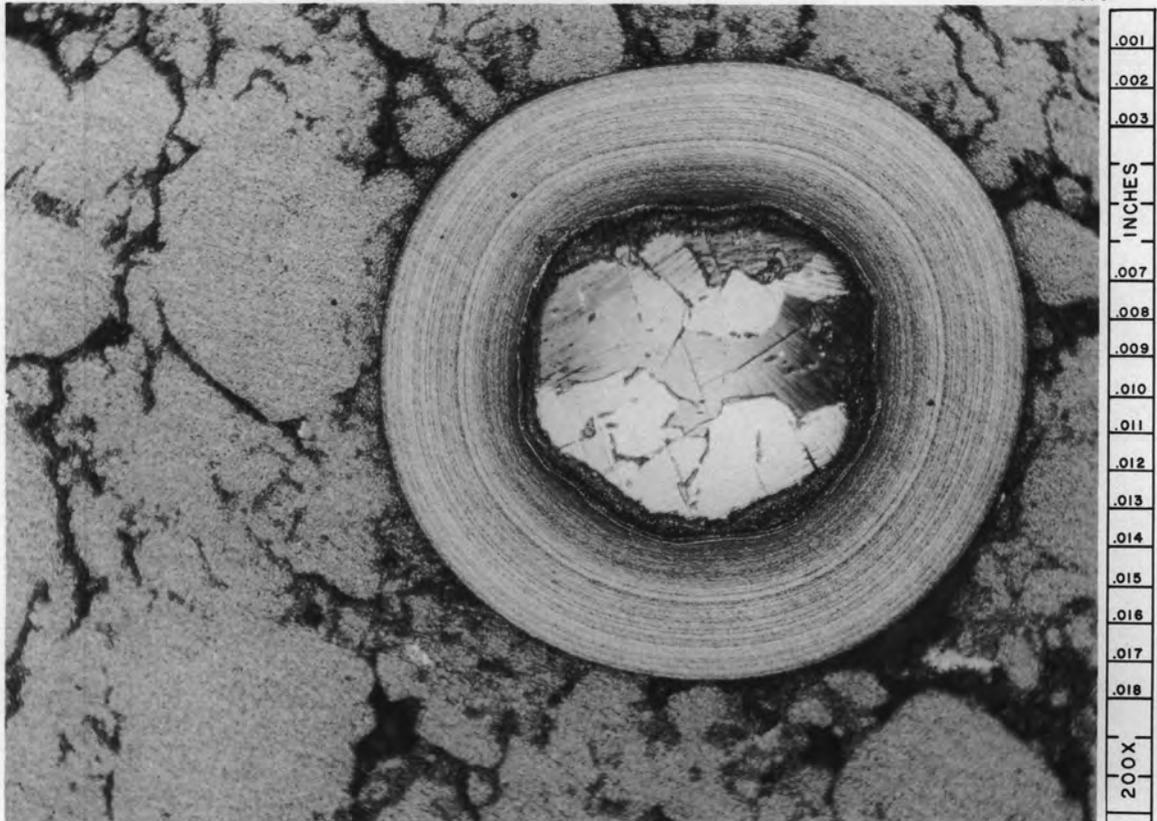


Fig. 14. Photomicrograph of Fueled-Graphite Element Containing Laminar-Coated Particles from Lot 3M-B1. Bright-field. Etchant: HAC, HNO₃, H₂O, 1:1:1.

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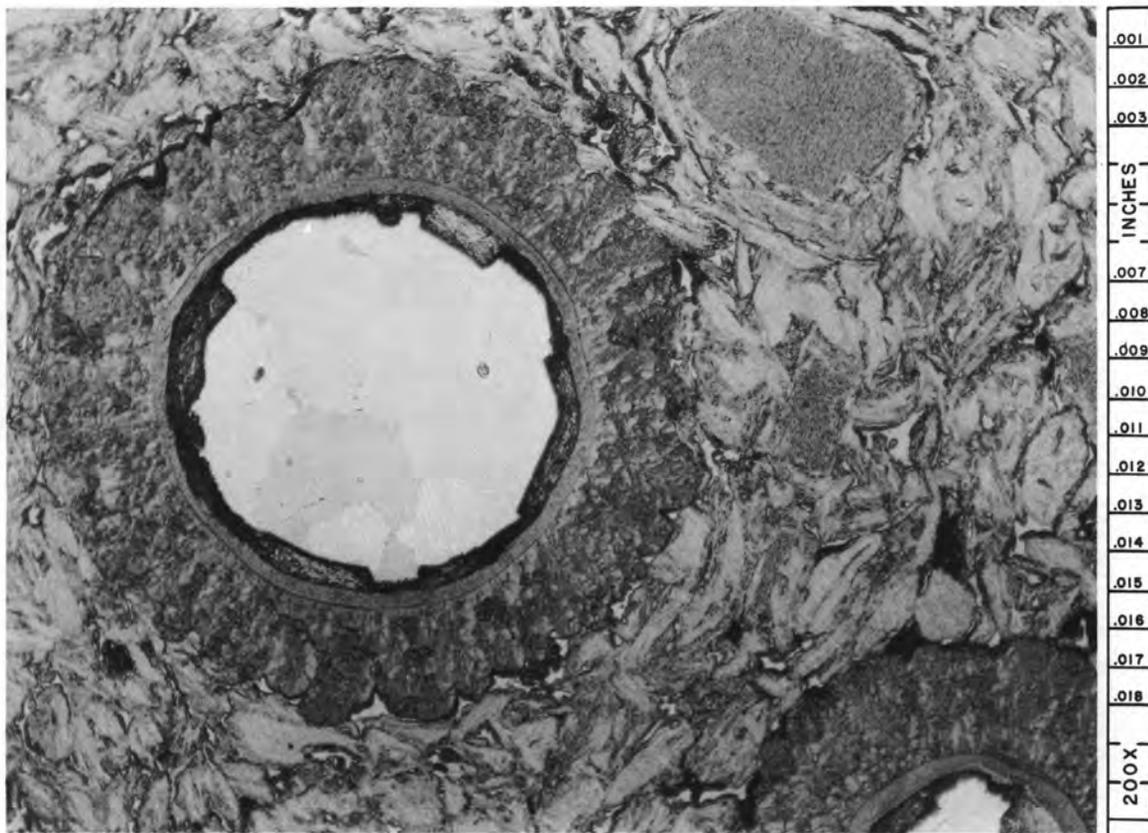


Fig. 15. Photomicrograph of Fueled-Graphite Element Containing Duplex-Coated Particles from Lot NC-B1. Bright-field. Etchant: HAC, HNO₃, H₂O, 1:1:1.

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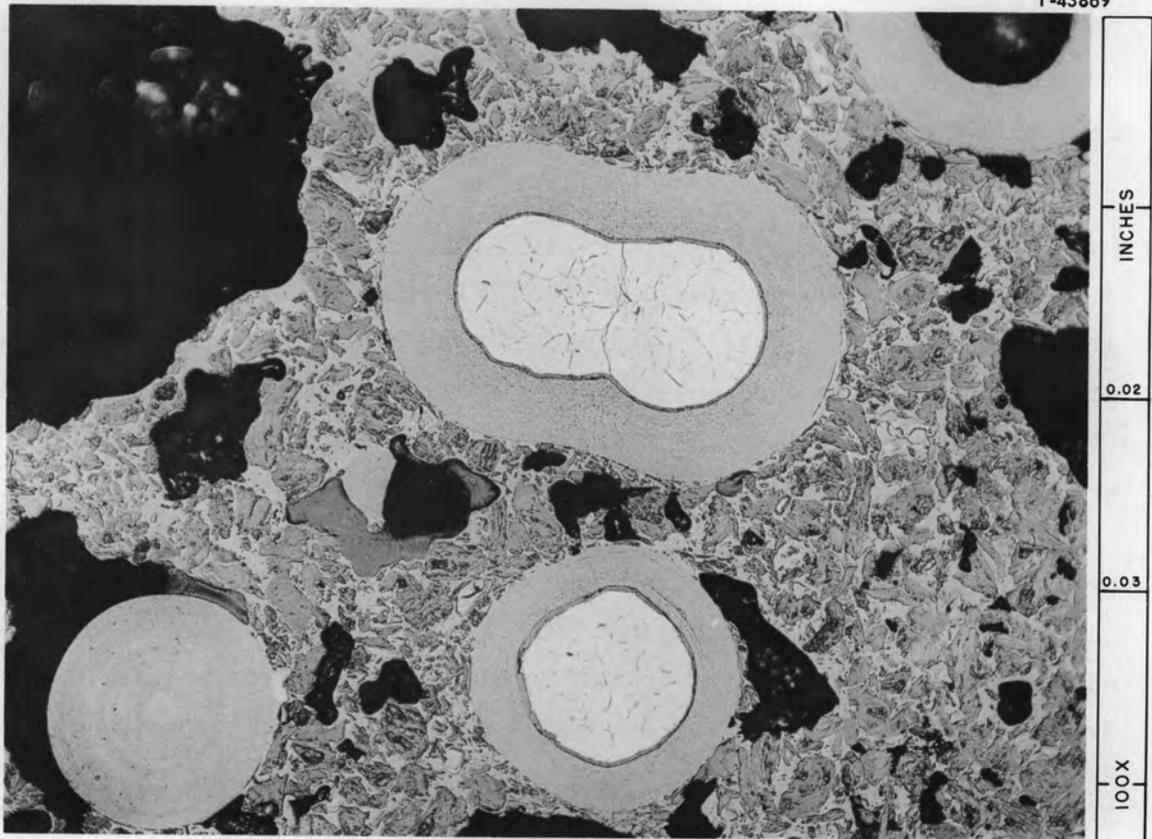


Fig. 16. Photomicrograph of Fueled-Graphite Element Containing Laminar-Coated Particles from Lot SC-B1. Bright-field. As-polished.

Fracture Strength. The fracture strengths of bushing-shaped elements, as determined in brittle ring tests, have ranged from 2000 to 4000 psi. The strength of elements with microstructures as shown in Fig. 14 was the lowest and that for elements with microstructures as shown in Fig. 16 was the highest. The mode of fracture in elements typified by the structure shown in Fig. 16 differed from the others in that the fracture path went through, not around, the coated particles.

Irradiation Tests (V. A. DeCarlo, C. W. Cunningham, Reactor Division; D. F. Toner, M. F. Osborne, Reactor Chemistry Division; R. E. Adams, E. L. Long, Metals and Ceramics Division)

Neutron-Activation Tests. Fission-gas release from neutron-activated elements is measured routinely at 1000°C for 24 hr. Under these conditions the release of Xe¹³³ has ranged from 5×10^{-5} to $8 \times 10^{-2}\%$, the higher values being associated with specimens containing approx 2% exposed fuel.³⁻⁵ Typical Xe¹³³ release values range from 10^{-3} to $10^{-2}\%$ or 10 to 100 times those from unsupported-coated particles.

It has been observed that heat treatments of 24 to 100 hr at 2000°C prior to neutron activation increase the Xe¹³³ release at 1000°C by factors of 2 to 10. In addition, bursts of fission gas have been detected when specimens heat treated in this manner after neutron activation have been exposed to moist helium at room temperature. This behavior is thought to be caused by uranium migration through the coatings at 2000°C followed by precipitation locally, possibly as UC₂, on cooling to room temperature where subsequent reaction with moisture damages the coatings and releases Xe¹³³.

Sweep Capsule Tests. Fueled-graphite elements containing coated particles have been irradiated in flowing helium in the MTR-48 and ORR-poolside sweep-gas facilities.

Two experiments, each involving cylindrical specimens approx 1 in. in diameter by 1 1/2 in. long, have been performed in the MTR-48 facility. In the MTR-48-5 experiment the test element contained a 1/8-in.-thick unfueled shell and was fueled with laminar-coated, spherical uranium carbide particles.^{3,4} It was irradiated initially at a central temperature of approx 2500°F to a burnup of approx 7 at. % of the total

uranium. Radiochemical analyses of the helium sweep gas showed that the fission-gas-release rates increased continuously during this period until apparently all of the particle coatings had failed. The test was continued at lower temperatures (1600-2000°F) to a final burnup of 17 at. % of total uranium. The fission-gas-release rates were temperature dependent during this period and were steady during each constant-temperature exposure. Postirradiation examination revealed that all of the particle coatings had failed and that the unfueled shell had developed a small crack during the irradiation. It also was noted that a tantalum-sheathed thermocouple had become severely oxidized during the experiment, indicating that the sweep gas contained oxidizing impurities. Thus, the failures observed may not have been due to irradiation effects alone.

In the MTR-48-6 experiment the test element had no unfueled shell and contained laminar-coated, angular particles of thorium-uranium carbide (Th:U = 2.2:1).⁵ This element was irradiated in the temperature range 1300-2000°F to a burnup of 1.6 at. % of Th + U. It was observed that the coatings were particularly susceptible to damage during temperature changes, and postirradiation examination showed that 10% of the particle coatings were cracked. As noted in the previous test, metal components in the assembly were partially oxidized.

Twelve bushing-shaped elements, 0.6-in. -OD × 0.25-in. -ID × 0.5-in. long, have been irradiated in each of three ORR poolside sweep capsule tests.⁴⁻⁶ Two types of elements have been tested, the first characterized as containing laminar-coated particles in a matrix of the type shown in Fig. 14, and the second as containing duplex-coated particles in a matrix such as that shown in Fig. 15. Two capsules, each containing one of the types of elements described, were irradiated with nominal central-fuel temperatures of 1700°F, and the third, containing laminar-coated particles, was operated at 2400°F. It was observed that the fission-gas-release rates in all three capsules were very sensitive to temperature changes. The elements in the third capsule were inadvertently thermally cycled from 2400 to 3210°F in 4 min. After this thermal cycle, a 100-fold increase

in the fission-gas-release rates was observed at 2400°F. A second capsule, also containing elements fueled with laminar-coated particles, was thermally cycled at the same time from 1700 to 2450°F with similar results.

The capsule containing elements with the duplex-coated particles was irradiated in the temperature range 1560-1760°F, with an average temperature of approx 1700°F, to a burnup of 9 at. % of the total uranium. The fission-gas release rates for these elements were 20 to 30 times higher than those for the unsupported duplex-coated particles irradiated at 1700°F in the ORR B9-8 experiment. It is important to note that because of differences in deposition conditions, these two batches of particles were not identical. For the unsupported particles, for example, the nominal thickness of the inner laminar layer, which is exposed to fission recoils, was 25 μ . For those in the fuel elements, however, this thickness was only 12 μ . In addition, more temperature changes and cycles were experienced by the graphite fuel elements than by the unsupported particles.

Postirradiation examination of these capsules is not complete. The capsule in which the elements containing laminar-coated particles were tested at 1700°F has been visually examined. Four of the twelve elements were found to be cracked, a result which was unexpected in view of the fact that graphite-matrix elements have been irradiated without failure at much higher power density conditions ^{1,2,3} than those used in these tests. The cracking may be the result of the relatively low strength of this particular type of element. It should be noted that these elements received a rapid thermal shock from 1700 to 2400°F and back to 1700°F during the irradiation test.

Summary and Discussion

Evaluation studies on fueled-graphite specimens have shown that coated-particle fuel elements can be fabricated without excessive damage to the particle coatings and that they meet acceptable specifications with respect to dimensions, fuel loading, bulk- and net-carbon density, and rupture strengths. The performance of the fueled-graphite elements has not been as outstanding as that of the unsupported particles tested in this program. In this regard the following points are felt to be

significant: (1) duplex-coated particles of the exact type which showed superior performance in the unsupported condition have not been used in the fueled-graphite specimens; (2) temperature variations and cycles have been more numerous in the experiments on fueled-graphite specimens; and (3) there is evidence that the level of gaseous oxidizing impurities has been higher in tests on the fueled-graphite specimens.

SUPPORTING RESEARCH

Diffusion of Uranium in Pyrolytic Carbon

(C. M. Blood and R. B. Evans III, Reactor Chemistry Division)

There are several mechanisms by which solid reactor fuel materials can diffuse through carbon or graphite matrices at high temperatures. However, only solid-state diffusion mechanisms need be considered for the special case represented by acceptable pyrolytic-carbon coatings on carbide fuel particles. Such coatings should exhibit an extremely low gas-permeability coefficient even after considerable fuel burnup has occurred. The results of the present studies should be most applicable to situations wherein the coating integrity is maintained, a solid-state diffusion mechanism controls fuel migration, and migration is contained within the coating. Particles with cracked (or otherwise violated) coatings are excluded by this characterization.

The objective of this section is to review the progress attained to date on an experimental investigation of the diffusion of uranium into massive columnar-pyrolytic carbon from an intimately contacted uranium carbide source.

Basic Considerations

Applicable Diffusion Equations. For ease and brevity of discussion, one might consider first the various diffusion relationships which describe the experimental results and also enable one to utilize the experimentally determined parameters for estimation of the migration rates. A rather general boundary condition has been selected for migration in both experimental and actual cases; namely, that the diffusion takes place as it would in a semi-infinite medium. This means that slow migrations have been anticipated for acceptable coatings and that the uranium concentration at the external surface will be zero for long periods of time for specified boundary conditions.

There are three types of equations to be considered. One gives the uranium concentration profile, a second gives the instantaneous rate of migration, and a third gives the total amount of uranium present in the pyrolytic carbon. The second is of little interest because transient conditions prevail; only the first and third equations are needed to describe experiments that are restricted to isothermal and unidirectional flow conditions. Under the conditions cited, the concentration, C , at any time, t , and position, x , takes the form

$$C(x,t) = C_c F(x,Dt), \quad (1)$$

where C_c is a parameter determined by the method of uranium placement at $x = 0$, and D , in cm^2/sec , is a diffusion coefficient. Sometimes experimental limitations preclude measurements of $C(x,t)$ at a point and one must utilize an integrated form of Eq. (1) which gives the total amount of diffused material within a finite interval, Δx or (x_2-x_1) , after a particular exposure time, t' . This relationship is

$$M(t') = A \int_{x_1}^{x_2} C(x,Dt') dx, \quad (2)$$

where $M(t')$ is the amount of diffused material, in grams, within Δx , and A , in cm^2 , is the area normal to flow. Classical solutions to Eqs. (1) and (2) are common knowledge. It is not immediately clear, however, whether these solutions apply in fact to the diffusion of uranium in pyrolytic carbon, or whether there exists a set of boundary conditions suitable for both the experiments on massive specimens and the conditions within a pyrolytic-carbon-coated uranium carbide particle.

Diffusion Coefficients (D). Frequently, the only results required from the experiments are a set of diffusion coefficients at different temperatures. Such would be the case if one were interested in impurity atom diffusion as represented, for example, by fission-product migration where the usual procedure is to assume that self-diffusion behavior is approximated and that a trace-layer technique may be employed. This technique is characterized by the placement of a small amount of material, Q_0 (g/cm^2), on the surface at $x = 0$ whereby C_c takes the form $(Q_0)/(\pi Dt)^{1/2}$, and $F(x,Dt)$ becomes $\exp [-(x)^2/(4Dt)]$. Equation (2) is

given by various forms of the error function [$\text{erf}(u)$ or $\text{erfc}(u)$] with the argument u given by $(x)/[2(Dt)^{1/2}]$. The attractive feature of this method is that direct determinations of $C(x,t)$, $M(t)$, and, particularly, Q_0 are not required, because D can be obtained from the slope of a semilog plot of various quantities [directly proportional to $C(x,t)$] vs x^2 .

But this is not the case when it is desirable to align the experimental conditions according to those which might exist within coated particles, where at least one of the coating surfaces is always in contact with uranium carbide. An applicable boundary condition for an analogous experiment would be maintenance of a constant potential at $x = 0$, that is, $C_c = C_0 \neq f(t)$. This quantity appears in both Eqs. (1) and (2). In this case, $F(x,t)$ is given by $\text{erfc}(u)$. The important point is that one must have values of C_0 to define migration rates within particle coatings; thus two parameters must be determined by experimentation.

Diffusion Potential (C_0). The relative importance of the C_0 term may be established by comparing the present investigation with conventional diffusion studies (for example, either self-diffusion in single crystals or the interdiffusion of two unlike gases). The conventional studies involve well-characterized systems for which C_0 may be readily defined. For example, the state of the diffusing material is known, equilibrium phase relationships are generally available, and the potentials for diffusion are well defined. In these cases, most of the applicable equilibrium phenomena will have been worked out before hand. In the present investigation, however, one is forced to proceed (perhaps prematurely) without the basic information related to C_0 . Thus, the present study is, of necessity, a pseudophase study coupled with a determination of diffusion rates. The determination of C_0 poses a most difficult problem and recognition of this fact is strongly reflected in the experimental procedures adopted. The present approach is to consider C_0 as being of primary importance with D taking a secondary role.

At present, C_0 is envisioned as being associated with some sort of saturation value of uranium in carbons or graphites that are contacted by uranium carbide. This saturation value or "apparent solubility" will

probably depend heavily on both temperature and structure. An experimental determination of C_0 is the primary objective of this investigation because this parameter represents the driving potential for the uranium diffusion process within particle coatings.

Materials and Experimental Procedure

Pyrolytic-Carbon Specimens. The pyrolytic carbon utilized was obtained from High Temperature Materials, Inc. The deposition conditions used in preparing the pyrolytic-carbon specimens are not precisely known; however, the structure and properties of these specimens are comparable to those for pyrolytic carbon deposited at 2000°C in methane at a total pressure of 20 mm Hg. The overall properties of the material are very similar to those of the large conical or columnar grains which constitute its microstructure. The crystallographic "c" directions in the columnar grains are essentially perpendicular to the (planar) deposition surface used in the manufacturing process; the "a" directions, therefore, are parallel to this surface. The vertices of the conical or columnar grains are situated at or near the deposition surface. The material is very dense with essentially zero open porosity.

In the columnar-type particle coatings, uranium diffusion proceeds from the initial layers (or cone vertices) and through the coating in the "c" direction. The diffusion specimens are fabricated with this orientation in mind. This is an important point since the results obtained elsewhere^{1,2} indicate that migration in the "c" direction takes place along the conical surfaces or grain boundaries. It is also important to note that the structure in the massive specimens utilized in the present (or similar) investigations is not necessarily closely related to the structures that exist in coatings on fuel particles. For example, several coated particles may be placed in the cross section of a single cone of a massive specimen.

Fabrication of Diffusion Couples. The experimental procedures are based on several requirements mentioned in the previous sections. In review, it is desirable that (1) the pyrolytic carbon contacts a large source of uranium carbide during the diffusion heat treatments, (2) the diffusion is unidirectional, and (3) the specimen is of convenient size and shape for subsequent examination and analysis.

^{1,2}J. R. Wolfe et al., "Self Diffusion of Uranium, Nickel, and Silver in Pyrolytic Graphite," March 15, 1962 (work performed under USAEC auspices) UCRL-6827T, -6828T.

The starting materials for couple fabrication consist of two plates or coupons of pyrolytic carbon, 0.2 in. × 0.2 in. × 1.5 in., and a strip of uranium metal approximately 0.001 in. thick. The metal is placed between the graphite coupons and is converted to UC by heating at 1300°C under vacuum for 2 hr in a graphite-resistance furnace. In order to effect a rapid conversion from UC to UC₂, the temperature is then raised to 2100°C for periods not greater than 2 hr. The amount of uranium diffusion into the pyrolytic carbon is negligible from the standpoint of detection; it is not zero, however, because the two coupons are firmly joined by the carbide layer, which indicates that some small amount of diffusion must have occurred. After fabrication, all exposed surfaces are subjected to a cleaning operation to minimize effects of contamination during fabrication. The couple is carefully dimensioned after cleaning.

Diffusion Heat Treatments. For the diffusion heat treatments, the couples are placed in an uncontaminated (new) holder, returned to the resistance furnace, and heated in vacuum for long-time periods at a selected temperature within the range 1700 to 2100°C.

Determination of Uranium Penetration. When the heat treatment is completed, the diffusion couple is removed from the furnace and a large portion of one coupon is removed by means of a small milling machine. Next, a wedge of the couple is removed in such a manner that the exposed surface may be represented by an inclined plane which passes through the uranium carbide layer and out through the adjacent coupon. It is possible to lay a photographic film on the inclined plane and obtain some autoradiographic information about the concentration profile. However, the current objective is to determine C₀ as well as D; accordingly, this technique has been bypassed and the angle, ϕ , of the inclined plane with respect to the original interface is merely recorded.

The specimen is then sectioned by removing incremental volumes which are cut 90 deg to the original interface. The uranium content of each section is determined by wet chemical analysis. (Activation techniques have been utilized and are still under consideration.) Although the precision associated with the wet analyses is somewhat disappointing, it is felt that one of the two analytical procedures mentioned should yield the best absolute values of M and C₀. Based on the angle, ϕ , the

dimensions of the increments, and the analytical results, one can prepare plots of the experimental data in terms of M/A , the weight of uranium remaining¹³ per unit area parallel to the original interface, versus the location, x , of the increment (or the surface of the cut) with respect to the interface.

Results

Status of Experimental Program. Ten couples have been subjected to various phases of the overall procedure; however, complete results are available for only five of the ten. Three of the five experiments completed represent "blank runs" (no diffusion heat treatment) to determine the effects of fabrication procedures on $C(x,0)$, that is, the initial concentration profile. The results of the "blank runs" indicated that the carbide/carbon interface is sharply defined. It was concluded, therefore, that the migration of uranium during fabrication is negligible. Results for the remaining couples, each heat treated, are shown in Fig. 17. Although the amount of data is limited, several interesting features pertinent to the experiments are demonstrated by the curves on this figure.

Residual Uranium Content. The first point of interest in regard to Fig. 17 involves the residual or background uranium content which is associated with the horizontal portions of the curves. Starting at zero penetration, the curves follow a relationship such as Eq. (2) up to penetrations around 5×10^{-3} cm. At this point the curve becomes a horizontal line which is not given by Eq. (2); in fact, this line indicates that the concentration is zero at all values of x greater than 5×10^{-3} cm since the slope is zero in this region. A tentative interpretation of the horizontal lines is that they represent either a background associated with the analytical technique or a contamination of the back side of the couple. Recent analyses of the specimen holders suggest that it would be difficult to attribute the background value to a surface or vapor migration mechanism. In any event, reasonable curves may be obtained by subtracting the average background value from all of the experimental points and replotting these versus x .

¹³From this point on, the increment $(x_2 - x_1)$ referred to in Eq. (2) shall be $[(x \rightarrow \infty) - (x_1)]$.

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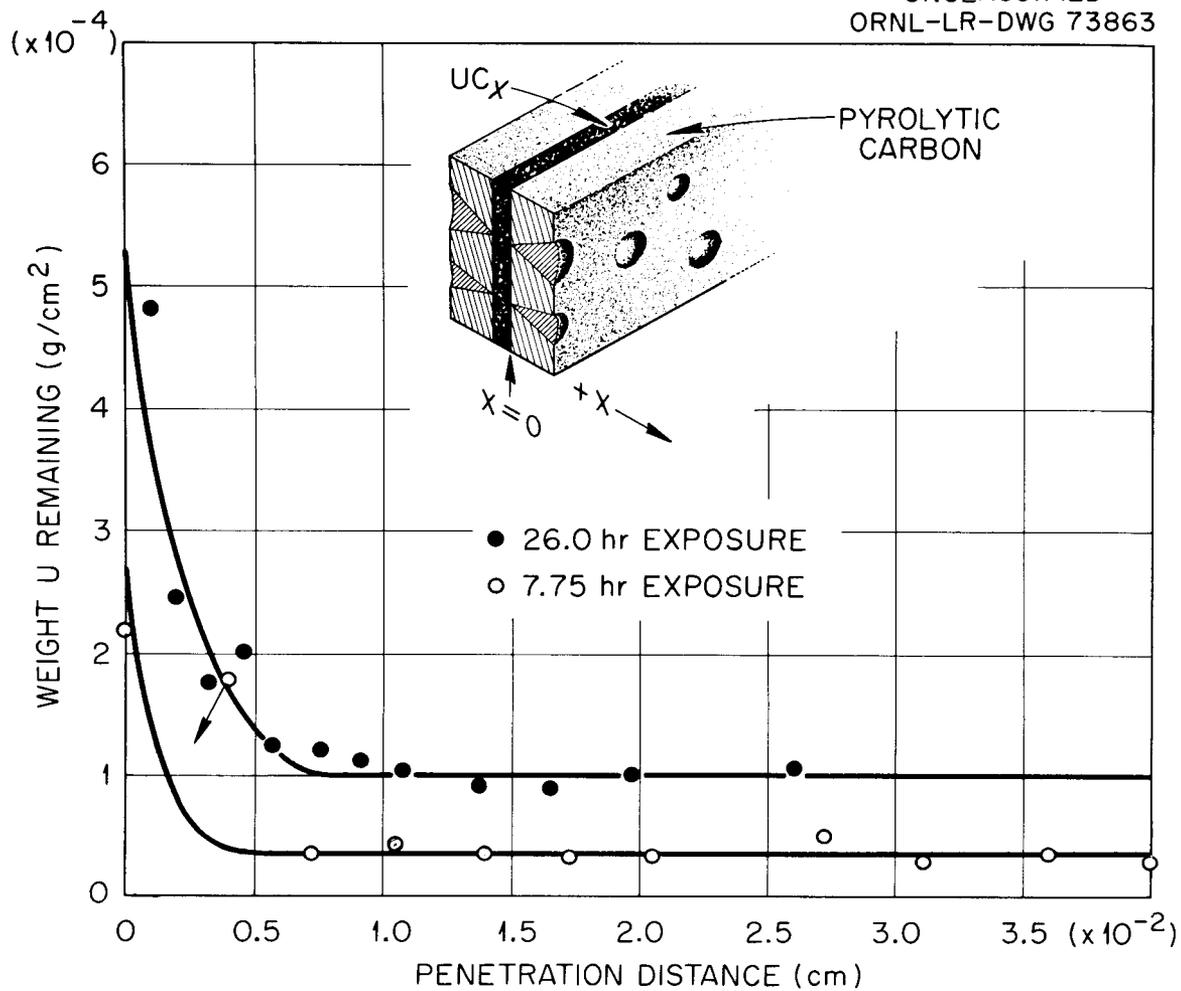


Fig. 17. Plot of Uranium Remaining, per Unit Area, as a Function of Distance from the Interface of Uranium Carbide - Pyrolytic-Carbon-Diffusion Couples Heated for 7.75 and 26.0 hr, Respectively, at 2100°C in Vacuum.

Computation of D and C_0 . The first and most difficult step in the correlation of the data involves the estimation of $x = 0$ and $[M(0,t)]/A$. At present, the interface can be located only to within one increment or approximately $\pm 15\mu$; this level of uncertainty, of course, leads to large errors in $[M(0,t)]/A$ values. Extrapolations of the data at $x > 0$ are the primary basis for these estimates. Once the values at $x = 0$ are selected and the background is subtracted out, the ratios $[M(x,t)]_{\text{exp}}/[M(0,t)]$ are computed and are plotted versus x . Comparisons of this plot with plots of the generalized function, $Y = (\pi)^{1/2} \text{ierfc}(u)$ versus u , where $u = (x)/2(Dt)^{1/2}$, yield an average value for D . One may calculate C_0 from the relationship $[M(0,t)]/A = 2C_0(Dt)^{1/2}$ once D is established.

Based on the data in Fig. 17 and the procedure given above, one finds that $D = 6 \times 10^{-11} \text{ cm}^2/\text{sec}$ and $C_0 = 0.162 \text{ g U/cm}^3$. The curves which appear in Fig. 17 are based on these values of D and C_0 and the known background value.

Tentative Conclusions. The relatively high value obtained for C_0 has been the most significant finding to date. This is clearly shown in Fig. 18 wherein plots of $C(x,t)$ versus x , based on the experimentally determined C_0 and D , are well within the range of direct measurement. The integral of the error function describes the total uranium transport; the error function describes the concentration profile; and the driving force for diffusion appears to remain constant with time. To obtain definitive results, heat-treatment periods should be increased from the range of 8 to 24 hr to periods of 200 to 1000 hr, depending on the temperature. Appreciable amounts of diffusion are observed because of the high C_0 value even though diffusion coefficients are low.

To obtain fundamental information from experiments of this type, microscopic techniques should be considered since preferred-region (conical-surface) migration is involved. The nature of the classical diffusion equations is such that the effects associated with this type of migration will be hidden in the parameters, C_0 and D . Regardless of the microscopic details, however, the experimental values of C_0 and D coupled with the equations will yield reasonable estimates of the migration behavior.

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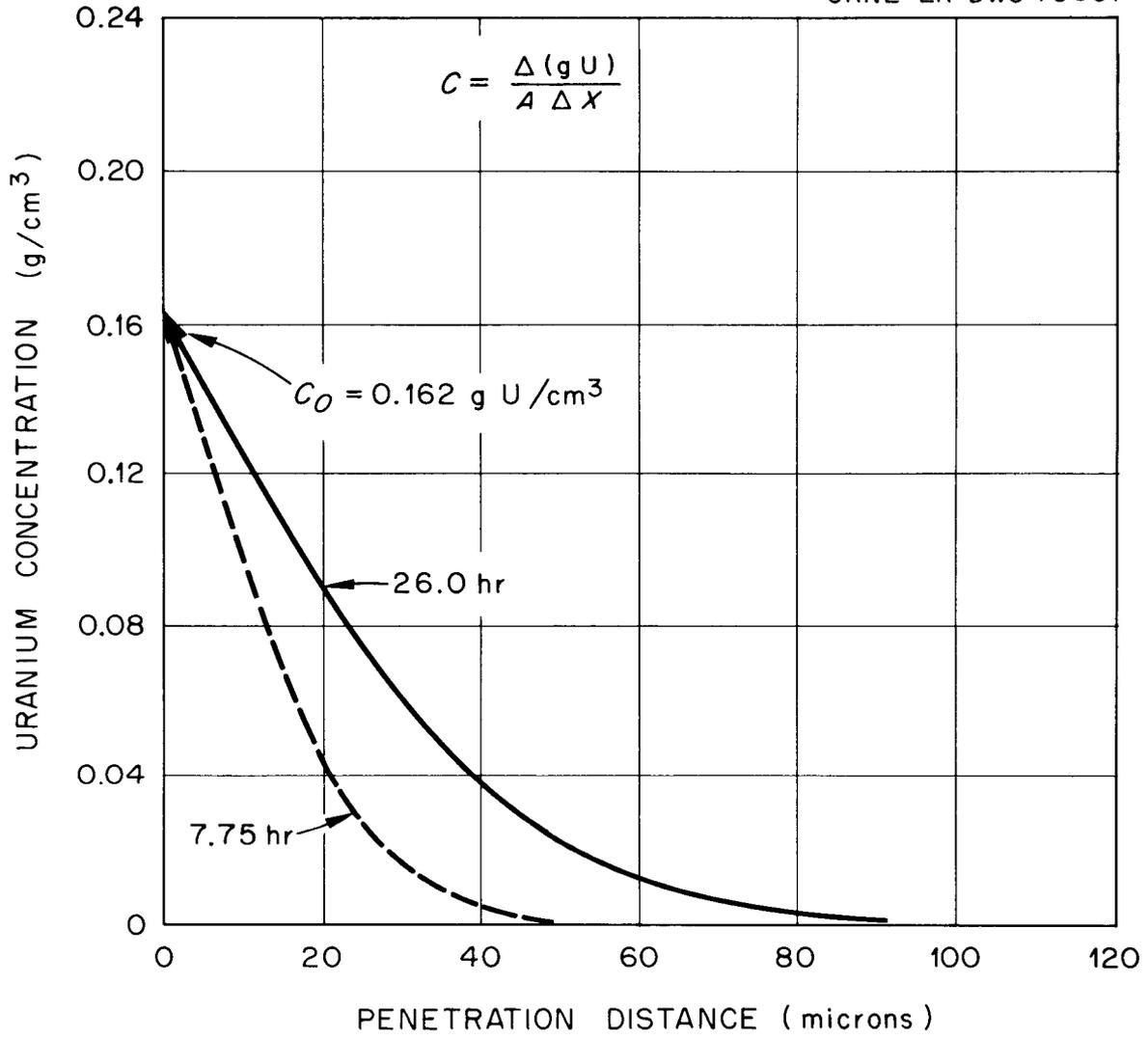


Fig. 18. Calculated Concentration Profiles.

Compatibility of Pyrolytic-Carbon-Coated Uranium
Carbide Particles With Water Vapor

(L. G. Overholser, N. V. Smith, and J. P. Blakely,
Reactor Chemistry Division)

These studies were undertaken to establish the rate of reaction of pyrolytic-carbon coatings on various lots of coated-uranium carbide particles with water vapor at approx 1000°C. In addition, the incidence of coating failure under these conditions, as determined by a HNO₃ leach test, was to be established. Studies of this type are of interest in high-temperature, gas-cooled reactor programs, since accidental in-leakage of water and subsequent contact with the hot coated particles is a potential hazard. All materials studied were supplied by the 3M Co. and the coatings were of the laminar type.

Tests at 900°C, Low H₂O Content

In the initial experiments coated particles from lots 3M-D and 3M-F were exposed at 900°C to flowing helium containing H₂O at a partial pressure of 20 mm Hg (total pressure, 1 atm). The gas was passed downward through a bed of the coated particles at a flow rate of approx 100 cm³/min and the resultant weight change was determined. The results are given in Table 3. The weight of coating in a given batch was determined by difference using the uranium content and assuming that the uranium was present as UC₂. Amounts and rates of coating removal were calculated accordingly. The reaction rates listed represent average values for the indicated exposure times. The quantities of uranium leached from the particles by 8 M HNO₃ at 90°C for 8 hr following the tests were established by chemical analyses of the leach solution.

The results show that the loss in weight of the coated particles was greater in all cases for lot 3M-D than for lot 3M-F. On the other hand, after the test exposures more uranium was leached from 3M-F particles than from 3M-D particles. These data indicate that the extent of the damage, which may be associated with a different mode of attack, actually was greater for lot 3M-F than for lot 3M-D. Irregularities in the coatings giving rise to thin coverage also could be responsible. Microscopic examination revealed only a shallow attack on the outer region of the coatings.

Table 3. Reactivity of Pyrolytic-Carbon-Coated Particles from Lot Nos. 3M-D and 3M-F
 With Helium Containing H₂O at a Partial Pressure of 20 mm Hg (Total Pressure, 1 atm) at 900°C

Sample No.	Weight of Sample (g)	Time (hr)	Weight Loss (g)	Calculated Amount of Coating Removed (%)	Calculated Rate of Coating Removal (g/g-hr)	Uranium Removed by HNO ₃ Leach	
						(g)	(% of Total U)
3M-D-3	2.01	8	0.018	3.5	0.004	0.0005	0.04
-4	1.66	24	0.040	9.4	0.004	0.001	0.09
-2	1.85	50	0.070	14	0.003	0.008	0.6
-1	1.79	100	0.070	15	0.002	0.009	0.8
3M-F-3	1.61	8	0.002	0.8	0.001	0.001	0.08
-4	1.96	24	0.005	1.3	0.0006	0.004	0.3
-2	1.56	50	0.008	2.7	0.0005	0.030	2.5
-1	2.05	100	0.021	5.3	0.0005	0.027	1.8

Tests at 700 to 1000°C, Intermediate H₂O Contents

Samples from lots 3M-113 and 3M-114 were exposed at 1 atm to helium containing H₂O at partial pressures of 50 to 350 mm Hg at 700 to 1000°C, leached with 8 M HNO₃ (as described previously), and examined microscopically. The results listed in Table 4 show that, as anticipated, the reaction rates increased with increasing temperature and steam pressure. The apparent order of the reaction was less than one under the conditions of these experiments. The reaction rates observed at 800, 900, and 1000°C are in good agreement with extrapolated data of Pilcher, Walker, and Wright.¹⁴ The one run at 700°C showed that the rate of attack is extremely slow at this temperature. This suggests that prolonged exposure would be required to cause serious damage to the coatings at temperatures of 700°C and below.

The data indicate that lot 3M-113 is more susceptible to damage than lot 3M-114. For example, in runs 3M-113-4 and 3M-114-6 the quantities of coating removed are comparable, but much more uranium was leached from 3M-113-4. The coatings on lot 3M-114 apparently are more protective after serious attack than are the coatings on lot 3M-113. Metallographic examination of a number of samples of these particles provides some explanation of this difference in behavior. In Fig. 19a the mode of attack on lot 3M-113 particles is shown to be quite localized. This same type of attack at a more advanced stage is shown in Fig. 19b, where pits are seen in many of the coatings. This type of attack would result in exposure of the uranium carbide core without extensive removal of the coating. It is to be noted that a number of the particles show signs of only a superficial attack.

Examination of lot 3M-114 coated particles revealed a different mode of attack, as illustrated in Fig. 20. This series of figures shows the results of exposing these particles to increasingly more severe conditions. Figure 20a shows the superficial attack on the outer layer of the coating after 6 hr at 800°C, during which 3.3% of the coating was removed. The particles shown in Fig. 20b suffered a 14% loss of the coating after 6 hr at 900°C and show significant attack of several particles, including separation of the outer layer. This effect was accentuated as the degree of attack increased, as seen in Fig. 21a after 4 hr at 1000°C, during which 21%

¹⁴J. M. Pilcher, P. L. Walker, Jr., and C. C. Wright, Ind. Eng. Chem. 47, 1742 (1955).

Table 4. Reactivity of Pyrolytic-Carbon-Coated Particles from Lot Nos. 3M-113 and 3M-114
 With Helium Containing H₂O at Partial Pressures of 55-355 mm Hg
 (Total Pressure, 1 atm) in the Temperature Range 700 to 1000°C

Sample No.	Weight of Sample (g)	Time (hr)	Temp. (°C)	Partial Pressure of H ₂ O (mm Hg)	Weight Loss (g)	Calculated Amount of Coating Removed (%)	Calculated Rate of Coating Removal (g/g-hr)	Uranium Removed by HNO ₃ Leach	
								(g)	(% of Total U)
3M-113-6	2.16	6	700	355	0.0025	0.2	0.0003	0.0001	0.02
-5	2.18	4	800	355	0.041	2.6	0.006	0.0232	4.0
-3	2.47	6	800	355	0.108	6	0.010	0.0021	0.3
-4	2.56	7	800	355	0.203	11	0.016	0.147	22
-2	2.51	6	1000	355	0.450	25	0.042	0.654	97
3M-114-4	2.50	6	800	233	0.036	3.2	0.005	0.0031	0.3
-1	2.45	6	800	355	0.036	3.3	0.006	0.0107	0.9
-9	1.99	6	900	233	0.127	14	0.024	0.001	0.1
-10	1.95	6	900	233	0.121	13	0.023	0.001	0.1
-3	2.41	4	900	355	0.159	15	0.037	0.002	0.2
-2	2.56	6	900	355	0.211	18	0.030	0.0177	1.4
-8	2.01	4	1000	55	0.099	11	0.027	0.001	0.1
-7	2.03	4	1000	92	0.149	16	0.041	0.002	0.2
-6	2.02	4	1000	149	0.193	21	0.053	0.001	0.1
-5	2.43	4	1000	355	0.424	39	0.097	0.016	1.3

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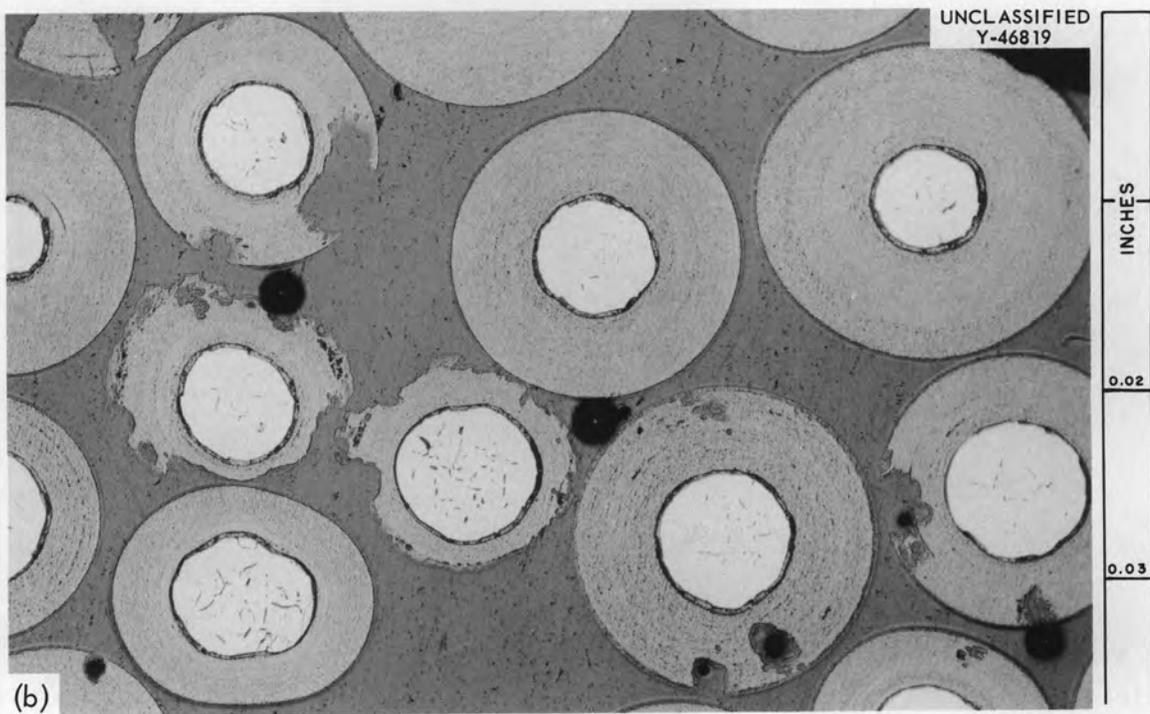
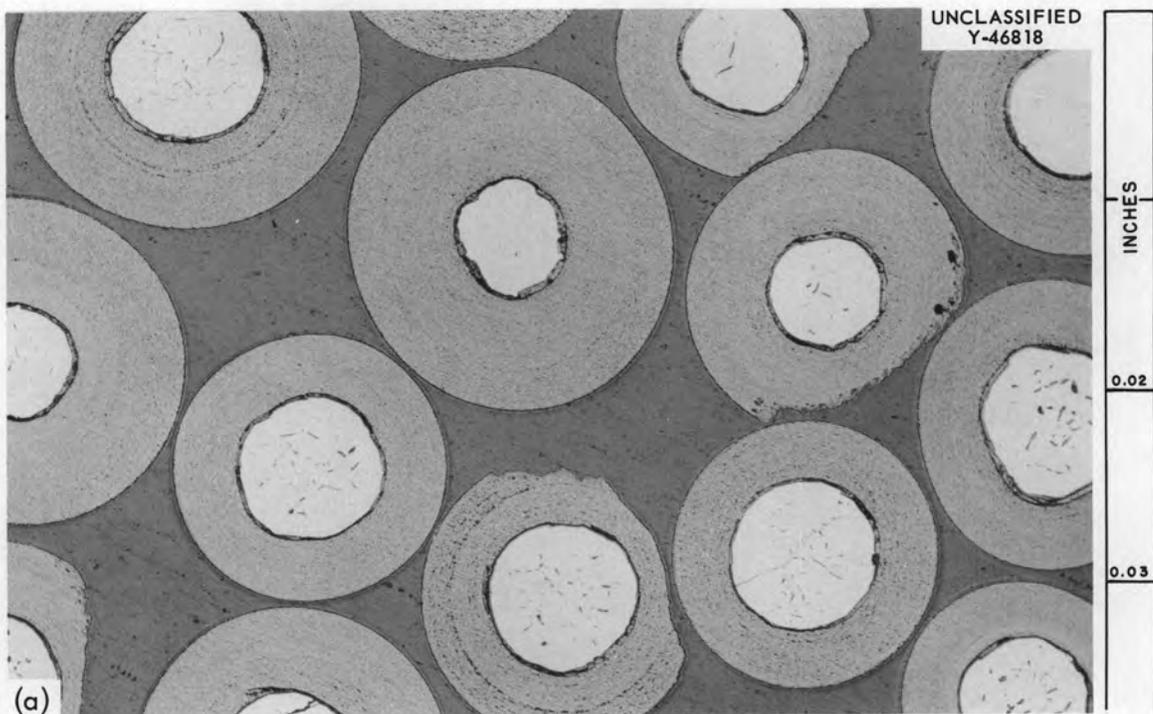


Fig. 19. Coated Particles from Lot No. 3M-113 Exposed at 800°C to Helium Containing H₂O at a Partial Pressure of 355 mm Hg (Total Pressure, 1 atm). a. Exposed for 6 hr; b. exposed for 7 hr. As-polished. 100X.

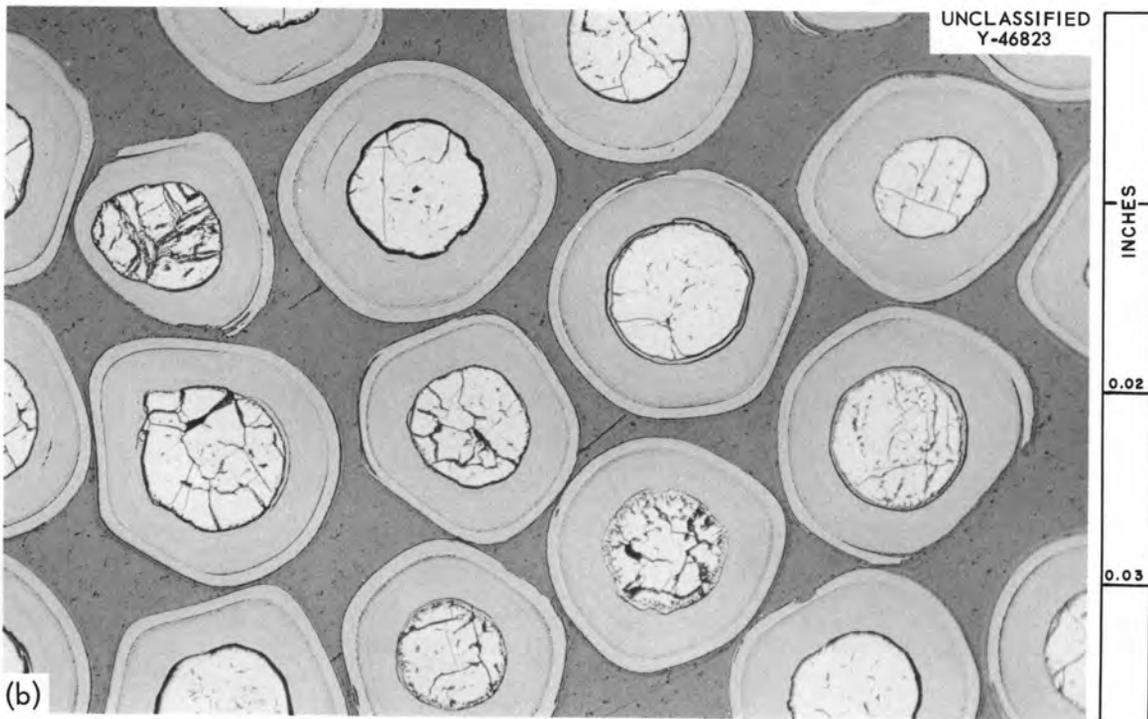
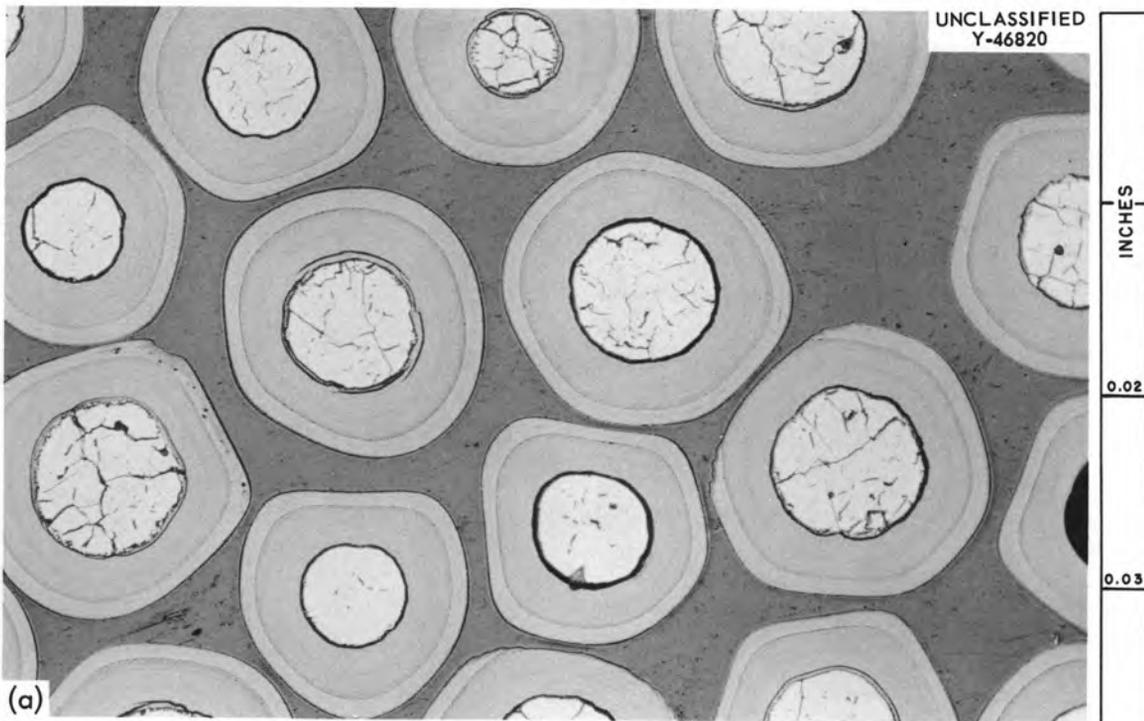


Fig. 20. Coated Particles from Lot No. 3M-114 After 6-hr Exposure to Helium Containing H₂O at a Partial Pressure of 233 mm Hg (Total Pressure, 1 atm). a. Exposed at 800°C; b. exposed at 900°C. As-polished. 100X.

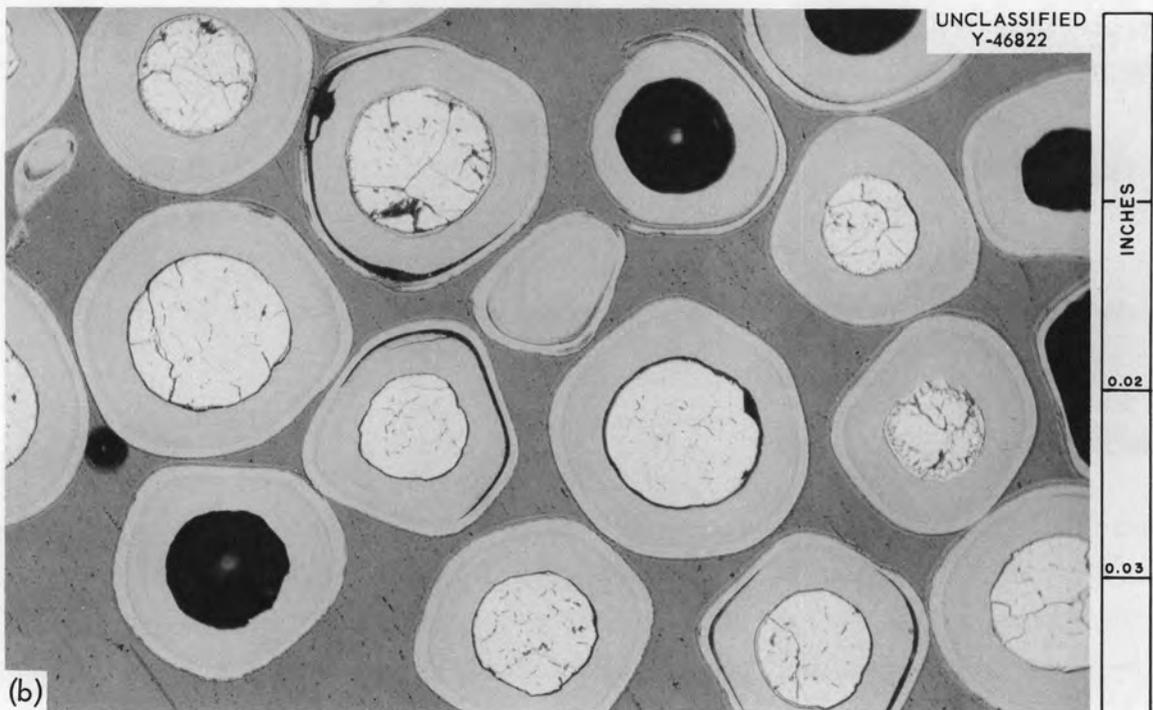
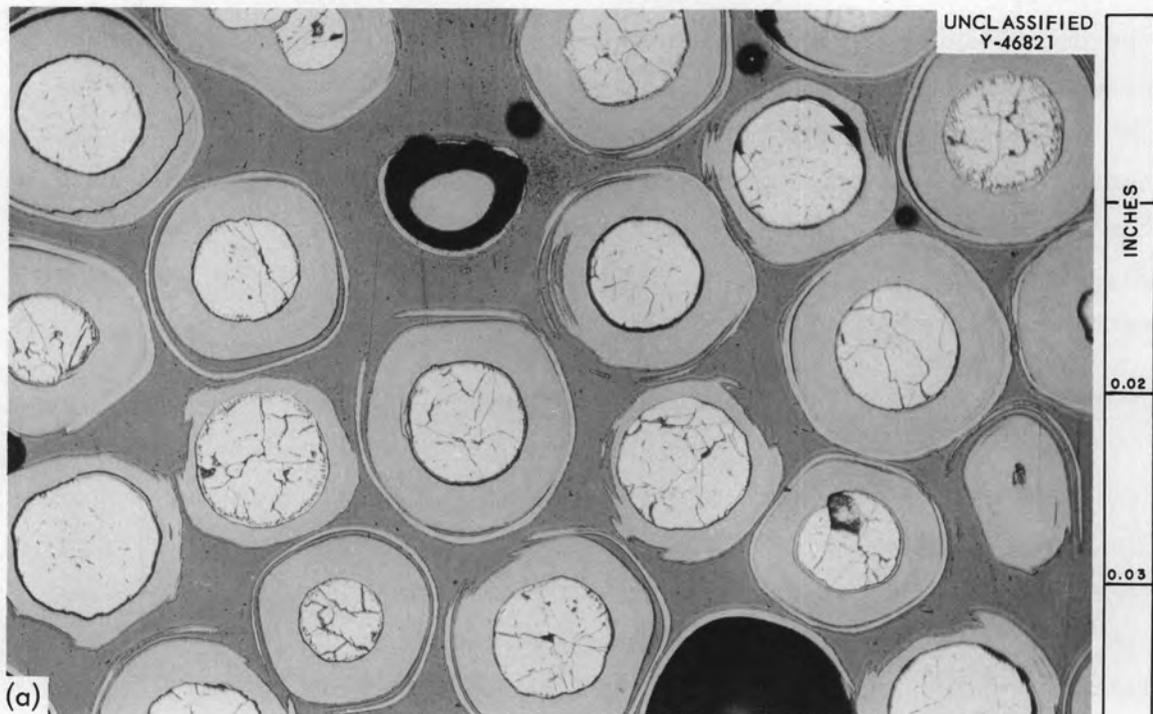


Fig. 21. Coated Particles from Lot No. 3M-114 After 4-hr Exposure at 1000°C to Helium Containing H₂O (Total Pressure, 1 atm). a. Partial pressure of H₂O of 149 mm Hg; b. partial pressure of H₂O of 355 mm Hg. Large dark areas are a result of fuel-particle removal during metallographic preparation. As-polished. 100X.

of the coating was removed. All particles were damaged and peeling of the outer layer was very evident, as illustrated in Fig. 21b, after an exposure of 4 hr at 1000°C at a higher partial pressure of H₂O. These latter conditions resulted in removal of 39% of the coating. In several cases most of the pyrolytic carbon was removed but no path was opened to the fuel particle. Generalized attack on coated particles from lot 3M-114 probably accounted for the protection afforded these particles even after substantial amounts of the coating were removed.

Tests at 800 to 1100°C, High H₂O Contents

More recently coated particles from lot 3M-117 were tested using, in some cases, higher partial pressures of H₂O and also higher temperatures. The results, presented in Table 5, indicate that the susceptibility of these particles to attack by steam is similar to that for lot 3M-114. The loss in weight of the two lots of particles at 900 and 1000°C are in fair agreement. The coatings in lot 3M-114 appear to be somewhat more protective than those in lot 3M-117, but both afford much better protection than was observed for lot 3M-113. Visual examinations of lot 3M-117 indicate that a pitting type of attack occurred.

Failure of a large number of the coatings occurred at 1100°C in the one run made at this temperature. It appears unlikely, therefore, that the coatings will remain intact at this temperature for as long as an hour when exposed to 1 atm of H₂O. At temperatures of 800°C and below, however, prolonged exposure may be permissible for some of the lots of coated particles.

Tentative Conclusions

The results of tests on five lots of pyrolytic-carbon-coated particles, all having the laminar type of coating, show marked differences in behavior that must be associated with different modes of attack by H₂O. Differences in reaction rates for different coatings have been observed at comparable exposure conditions. Furthermore, there is no clear-cut relationship between the amount of pyrolytic carbon removed from the coating and the incidence of failure of the coating as determined by the HNO₃ leach. This behavior suggests that it would be necessary to experimentally evaluate a particular lot of material before its compatibility with H₂O at 900 to 1000°C could be predicted with any degree of

Table 5. Reactivity of Pyrolytic-Carbon-Coated Particles from Lot 3M-117 with Helium Containing H₂O at Partial Pressures of 355-635 mm Hg (Total Pressure, 1 atm) in the Temperature Range 800-1100°C

Sample Number	Weight of Sample (g)	Time (hr)	Temperature (°C)	Partial Pressure of H ₂ O (mm Hg)	Weight Loss (g)	Calculated Amount of Coating Removed (%)	Calculated Rate of Coating Removal (g/g-hr)	U Removed by HNO ₃ Leach	
								(g)	Percent of Total U
3M-117-20	2.072	4	800	355	0.069	6.4	0.016	0.004	0.4
-16	2.102	1	800	635	a	a	a	0.001	0.1
-23	1.980	4	800	635	0.163	15.9	0.04	0.011	1.3
-5	2.056	1	900	355	0.030	2.8	0.028	0.027	3.0
-6	2.101	2	900	355	0.075	6.9	0.035	0.057	6.3
-22	2.063	4	900	355	0.115	10.9	0.027	0.032	3.5
-13	1.832	4	900	355	0.074	7.9	0.020	a	a
-17	2.028	4	900	355	0.142	13.5	0.034	0.053	5.9
-21	2.008	4.5	900	355	0.117	11.3	0.025	0.024	2.7
-8	2.132	1	900	635	0.078	7.1	0.071	0.006	0.6
-24	1.615	1	900	635	0.052	6.2	0.062	0.030	4.1
-7	2.012	2	900	635	0.172	16.6	0.083	0.037	4.1
-3	2.556	1	1000	355	0.084	6.4	0.064	0.050	4.4
-2	1.979	2	1000	355	0.186	18.3	0.092	0.122	14
-14	2.069	2	1000	355	0.179	16.8	0.084	a	a
-19	2.048	2	1000	355	0.133	12.5	0.063	0.031	3.4
-12	2.012	4	1000	355	0.417	40	0.10	0.061	6.8
-1	2.337	4	1000	355	0.521	43	0.11	0.046	4.5
-10	1.924	1	1000	635	0.114	11.5	0.12	0.036	4.1
-25	1.778	1	1100	635	0.421	46	0.46	0.32	40

^aNot determined.

certainty. It appears that prolonged exposure at 800°C and below may be permissible for some lots of coated particles; at 1100°C, however, it is unlikely that the coatings will remain intact for as long as 1 hr.

COMPATIBILITY STUDIES WITH LIQUID COOLANTS

(E. L. Compere, S. A. Reed, D. M. Richardson, and L. F. Woo
Reactor Chemistry Division)

The development of a variety of coated-particle fuel elements of promising quality for use in gas-cooled reactor systems suggested that a potential of high performance exists in liquid-cooled systems. The use of ceramic coated particles offers the possibility of good neutron economy and the capability of high temperatures and long burnup in liquid-cooled reactor fuels. The major questions concerning this application involve fission-product retention and compatibility.

The purpose of this phase of the program is to assess the compatibility problem, including the effects of gamma radiation, in a variety of liquid coolants. By general classification the liquids investigated are pressurized water, organic-moderator coolants, and molten fluoride salts.

PRESSURIZED WATER

In studies with pressurized water, the major emphasis has been on the effects of high rates of heat transfer on coated fuel particles and graphite matrices in flowing systems. Test materials have been special grades of unfueled matrix graphite and specimens fueled with alumina-coated UO_2 and pyrolytic-carbon-coated uranium carbide particles procured from National Carbon Company and Speer Carbon Company. Specimens of massive pyrolytic carbon and a high-purity, high-density spectrographic grade of graphite also have been tested for comparison with the matrix grades.

Heat fluxes of 300,000 to greater than 1,000,000 Btu/hr·ft² have been generated by electrically resistance heated, 1/4-in.-diam rod specimens immersed in flowing (2 to 6 fps) water at 225-300°C. The apparatus, shown schematically in Fig. 22, was specially designed for placement in a bypass line of a 100-gpm pump loop.

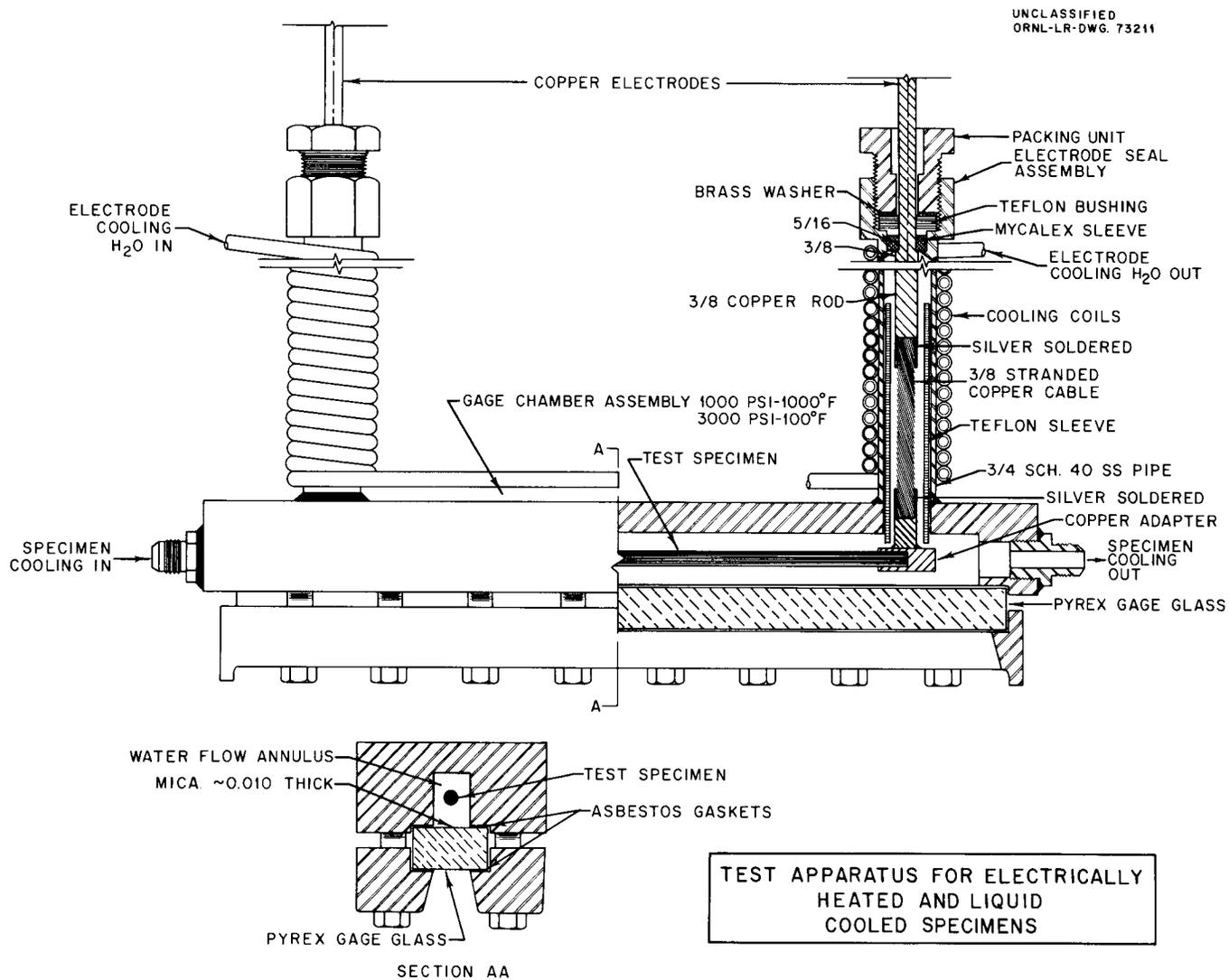


Fig. 22. Test Apparatus Used in Bypass Line of Pump Loop for Testing Compatibility of Electrically Heated Graphite-Base Materials in Flowing, Pressurized Water.

The pyrolytic-carbon specimens were machined from massive plate material in such a manner that the large, columnar grains were essentially perpendicular to the longitudinal rod axis. Thus, a wide range of crystallographic directions in this highly anisotropic material was exposed to the flowing water. A specimen of this type was not detectably attacked after a 24-hr exposure to water at 250°C, a flow velocity of 2 fps, and a generated heat flux of 500,000 Btu/hr·ft². However, under similar conditions but at a flux of 600,000 Btu/hr·ft² for 250 hr, mild attack occurred at the edges of the layered structure of the pyrolytic carbon. A third specimen, tested under similar conditions, splintered longitudinally as shown in Fig. 23 after 50 min at a flux of 860,000 Btu/hr·ft². Again, there was evidence of preferential attack along the layers of the structure.

A photograph of the spectrographic grade graphite specimen is shown in Fig. 24 after a 45-min exposure at a flux of 900,000 Btu/hr·ft² in 300°C water flowing at 2 fps. The attack on this specimen can be described as generally uniform with a rather more pronounced attack at a region near the downstream end. Calculations indicated that the critical (burnout) heat flux for the material probably was exceeded under the conditions employed. It is inferred that under film-boiling conditions the rod became so hot as to permit the steam-carbon reaction to proceed at a substantial rate.

Two specimens of unfueled grades of matrix graphite supplied by Speer Carbon Company were exposed at generated heat fluxes of approximately 1,000,000 Btu/hr·ft² under conditions which were essentially similar to those used for the spectrographic graphite specimen. Visual examination indicated that these specimens were not attacked during 250-hr tests.

In initial screening tests in static autoclaves, coupon specimens of several lots of conventional graphitized grades of nuclear graphite and experimental grades of extruded or molded types of matrix graphites were exposed submerged in nitrogen-sparged water at 320°C (1500 to 1600 psig) for 200-hr periods. Tests were completed with National Carbon Company graphitized grades AGOT, ATJ, CEQ, and TSX, and with special grades TS-148, TS-160, and FE-3, each of the latter grades having been baked at 1400, 2000, and 2800°C. Massive pyrolytic carbon furnished by High Temperature Materials, Incorporated, also was tested. In all cases, weight and dimensional measurements indicated that no attack occurred.

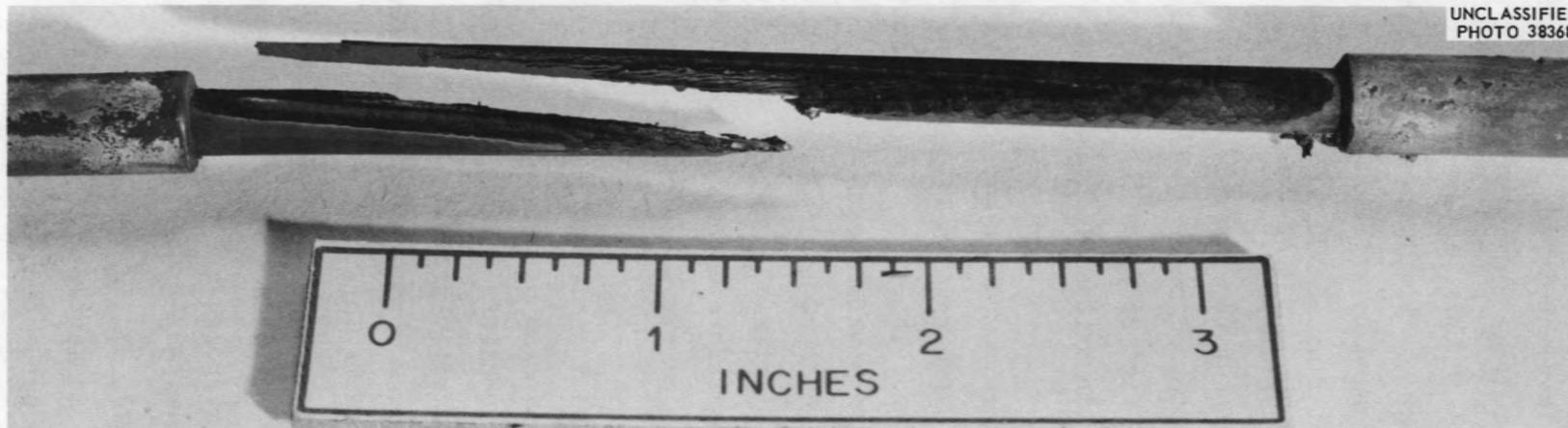


Fig. 23. Pyrolytic-Carbon Rod Which Failed After 50-min Exposure at a Heat Flux of $860,000 \text{ Btu/hr}\cdot\text{ft}^2$ in 250°C Water at a Flow Rate of 2 fps.

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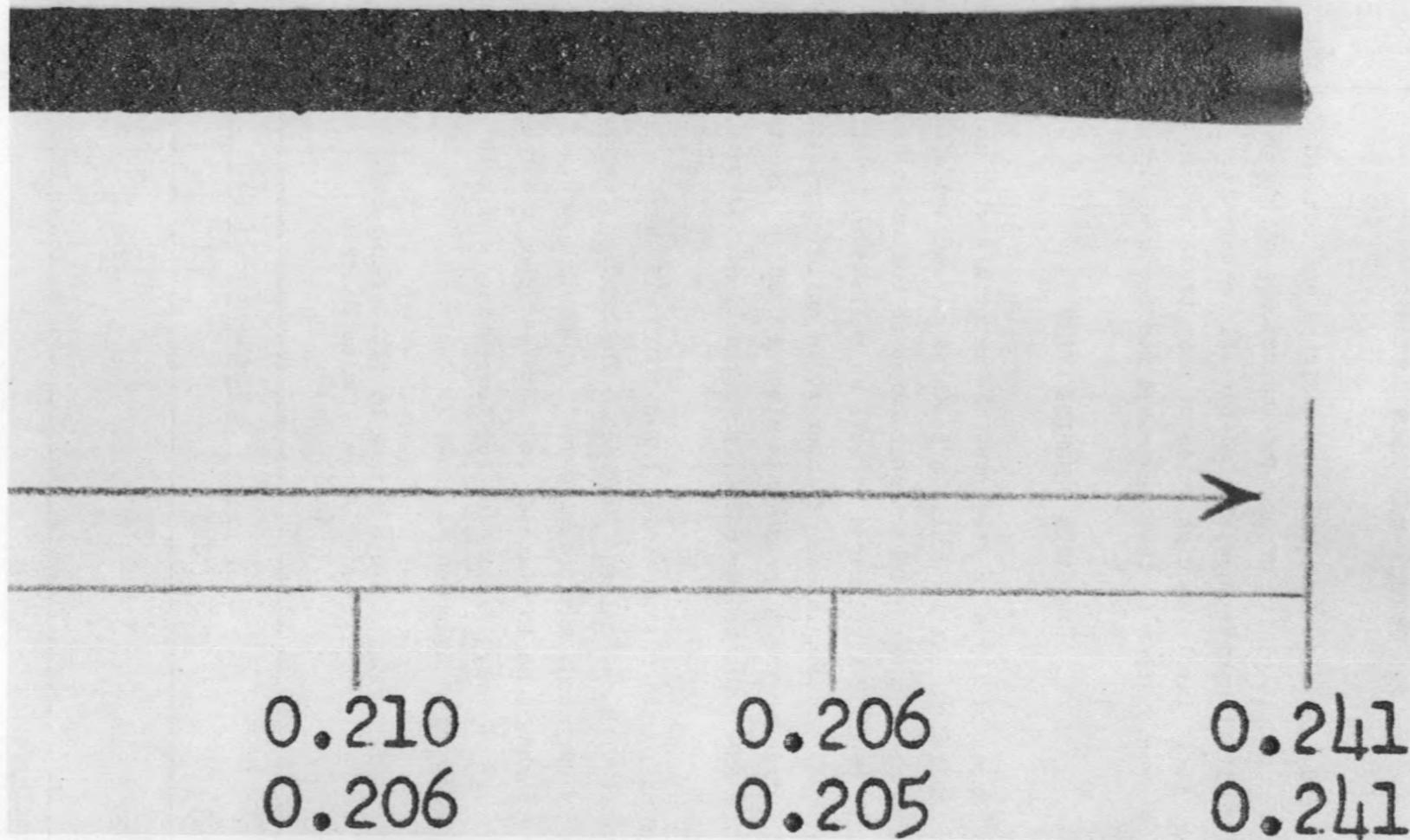


Fig. 24. Spectrographic Grade Graphite Specimen After 45-min Exposure at a Heat Flux of 900,000 Btu/hr·ft² in 300°C Water at a Flow Rate of 2 fps. Direction of flow is indicated by the arrow. The numbers denote mutually orthogonal diametral dimensions, in inches, measured after the test at the positions indicated.

ORGANIC-MODERATOR COOLANTS

A forced-flow test loop has been designed and constructed for studying the compatibility of organic-moderator coolants such as Santowax-R with graphite-base, coated-particle materials. With this apparatus, tests involving high rates of heat transfer can be carried out in a manner similar to that described for the pressurized-water tests.

MOLTEN FLUORIDE SALTS

The compatibility of coated-particle materials with molten fluorides has been studied in static crucible tests in vacuum and with helium and hydrogen as cover gases. Test temperatures in the range 800–1000°C were selected to produce accelerated effects as well as to investigate the region of hot-spot conditions of interest in nuclear reactors employing molten fluorides. The fluoride salt mixture used in almost all the tests was the LiF-NaF eutectic (mp 652°C) prepared by mixing pure, commercial materials.

Alumina-coated UO₂ particles (CP-2-NUMEC 915) were found to be incompatible with the molten fluorides. The coatings were either dissolved or severely corroded, and cracking was frequently observed. Alpha-alumina spheres, 1 mm in diameter and obtained from the Linde Company corroded more rapidly with increasing temperature and with increasing partial pressure of hydrogen as shown in Table 6.

Table 6. Average Attack by LiF-NaF Eutectic
on 1-mm-diam Alpha Alumina Spheres
(μ /100 hr)

Partial Pressure of H ₂ ^a (atm)	Temperature (°C)		
	800	900	1000
1	21	b	(spheres consumed)
1/20	0 ^c	29	b
0	0 ^c	13	b

^aTotal pressure, 1 atm.

^bNot determined.

^cSurfaces lightly etched; some cracks visible.

The alumina spheres were also tested in LiF-NaF-KF eutectic ("flinak") at 600°C with helium cover gas. The average attack was 38 μ in 100 hr. Since the "flinak" used had been especially treated to remove water and oxidizing impurities, the aggressive attack might have been due to the KF component or to FeF₂ and CrF₂ impurities.

Early tests of pyrolytic-carbon-coated fuel particles were performed concurrently with those for alumina spheres. The particles were placed on top of the salt and remained there throughout the test. (This behavior was indicative of nonwetting since the average particle density was greater than the density of the molten salt.) Under these conditions there was never any evidence of damage to the coatings.

Recent tests of pyrolytic-carbon-coated particles were conducted with the particles submerged in the salt in nickel crucibles at 900 to 1000°C for 200 hr in hydrogen at a pressure of 3 atm. The coatings were damaged and in some batches a stain identified as UO₂ was found on the bottom of the crucibles. Many particles were flattened where they contacted the nickel crucible. The coating damage observed is believed to have been due to carbon diffusion into the nickel as well as to the nickel-catalyzed reaction of carbon and hydrogen to form methane.

EFFECTS OF GAMMA RADIATION

The compatibility of liquid coolants with coated-particle materials could be substantially affected by irradiation. If fission products are contained, the effects would for the most part be limited to those associated with neutrons and gamma rays. Initial studies have been concerned with the effects of gamma radiation.

Irradiation of autoclaves containing coated particles and graphite-base materials has been carried out in a (nominal) 10,000-curie Co⁶⁰ source. The experimental apparatus, shown schematically in Fig. 25, is located in a corner of the source cavity. The dose rate is estimated to be 1.1×10^{-3} w/g of graphite (0.85×10^{18} ev/min·ml).

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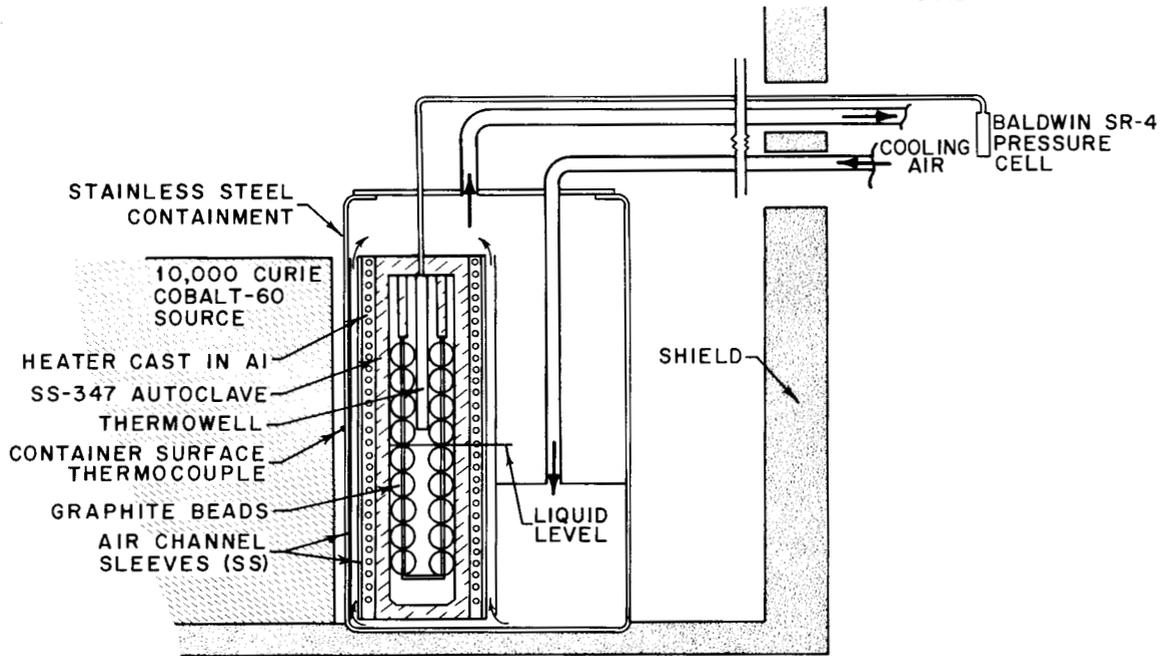


Fig. 25. Schematic Drawing of Gamma-Irradiation Experiment.

A 2155-hr test was completed on a type 347 stainless steel autoclave containing 1/4-in.-diam spheres of type AGOT graphite, pyrolytic carbon, and graphite mixes NCC grade TS-148 (baked at 2000°C) and NCC grade TS-160 (baked at 2000°C) in contact with D₂O pressurized with helium at 330°C. A small quantity of gas was generated during the test. This gas was collected and, based on the average of results of mass spectrometry and gas chromatography, was found to contain 132 μmole of CO₂ and 20 μmole of D₂; neither CO nor hydrocarbons were detected. These results are not consistent with those to be expected from the simple reaction of carbon with heavy water which would produce twice as much D₂ as CO₂. A selective sorption of D₂ in the graphite pores could account for this inconsistency. Microscopic examination of the surfaces of the spheres revealed that no significant attack had occurred. Diameter increases of 0 to 0.1% were observed.

An autoclave experiment is currently in operation to test the compatibility of coated particles and graphite-base materials with Santowax-R at 400°C in the presence of a gamma field. The autoclave contains spheres of the type described above for the D₂O tests pressurized with helium; in addition, there are two small, evacuated Pyrex capsules containing Santowax-R with alumina-coated UO₂ particles (CP-2-NUMEC 915) and pyrolytic-carbon-coated uranium carbide particles (CP-3-National Carbon 201). As of October 5, 1962, the test had been in operation for 1025 hr of which 1000 hr were at 400°C.

Another autoclave experiment is being fabricated for use in testing the compatibility of graphite-base materials with molten fluoride salts at 600°C in a gamma field. The INOR-8 autoclave is to be equipped with two helium-filled nickel capillary tubes for purging and sampling the gas phase during irradiation.

CHEMICAL PROCESSING OF COATED-PARTICLE FUELS

(L. M. Ferris, Chemical Technology Division)

Chemical processing of irradiated fuel elements is only one of the many steps in the overall fuel cycle and consists of dissolution of the fuel values, uranium and thorium, followed by a decontamination procedure to effect separation of these elements from the fission products.

Currently, extraction of the uranium and thorium from nitric acid solutions with tributyl phosphate is the best method for achieving the desired decontamination. Initial laboratory work has been concentrated on graphite-base fuels which contain either pyrolytic-carbon- or alumina-coated particles. At least five processing methods for these fuels are being evaluated. They are "grind-leach,"^{15,16} combustion-dissolution,¹⁶ the 90% HNO₃ process,^{16,17} anodic disintegration, and chloride volatility.¹⁸ A brief description of these techniques and a summation of the results obtained are presented below.

GRIND-LEACH PROCESS

This process involves mechanically grinding the fuel elements fine enough to ensure rupture of the particle coatings, and then leaching the resulting powder with nitric acid or HNO₃-HF to recover the uranium and thorium. This technique is applicable to all types of graphite-base fuel elements, the extent of grinding being dependent primarily on the size of the coated particles. In principle, the technique is applicable to other types of high-temperature reactor fuels, e.g., those having alumina or BeO matrices. When grinding is fine enough (-200 mesh for most coated-particle fuels), uranium and thorium are recovered almost quantitatively by leaching for 6 to 8 hr in a suitable boiling reagent. The results of a number of tests are given in Table 7.

¹⁵M. J. Bradley and L. M. Ferris, Nucl. Sci. Eng. 8, 432 (1960).

¹⁶L. M. Ferris, A. H. Kibbey, and M. J. Bradley, Processes for Recovery of Uranium and Thorium from Graphite-Base Fuel Elements, Part II, ORNL-3186 (Nov. 16, 1961).

¹⁷M. J. Bradley and L. M. Ferris, Ind. Eng. Chem. 53, 279 (1961).

¹⁸T. A. Gens, ORNL Chemical Technology Division, unpublished data.

Table 7. Uranium and Thorium Recovery from Fueled Graphite
by the Grind-Leach Process

(Fuel ground to -200 mesh and leached for 6 to 8 hr with boiling reagent)

Fuel	Composition of Fuel Body (wt %)		Leachant	Recoveries (wt %)	
	Uranium	Thorium		Uranium	Thorium
Uncoated UO ₂ -ThO ₂	1.2	8.0	13 M HNO ₃ -0.04 M HF- 0.1 M Al(NO ₃) ₃	99.9	99.9
Uncoated UC ₂ -ThC ₂	1.5	7.2	13 M HNO ₃ -0.04 M HF- 0.1 M Al(NO ₃) ₃	90	88
Alumina- coated UO ₂	8.0	--	15.8 M HNO ₃	99	--
Pyrolytic- carbon- coated UC ₂ -ThC ₂	9.7	33.8	15.8 M HNO ₃	98.8	99.9
Pyrolytic- carbon- coated UC ₂ -ThC ₂	9.6	33.5	13 M HNO ₃ -0.04 M HF- 0.1 M Al(NO ₃) ₃	99.4	99.9

Several engineering problems must be solved before this method can be considered practicable. The feasibility of finely grinding fuels containing refractories and abrasives such as SiC and alumina must be demonstrated. Methods for filtering or centrifuging large volumes of graphite slurries and for adequately washing graphite beds must also be developed.

COMBUSTION-DISSOLUTION PROCESS

Combustion, in oxygen, of graphite-base fuels containing carbon-coated fuel particles followed by dissolution of the oxide ash leads to quantitative recovery of uranium and thorium, as shown in Table 8.

Table 8. Uranium and Thorium Recovery from Fueled Graphite by the Combustion-Dissolution Process

(Fuel burned in oxygen at 750 to 850°C; ash leached 6 to 10 hr in boiling reagent)

Fuel	Composition of Fuel Body (wt %)				Leachant	Recoveries (wt %)	
	U	Th	Si	Fe		U	Th
Uncoated UC ₂ -ThC ₂	1.7	8.0	--	--	13 <u>M</u> HNO ₃ -0.04 <u>M</u> HF- 0.1 <u>M</u> Al(NO ₃) ₃	100	100
Pyrolytic-carbon-coated UC ₂ -ThC ₂	9.9	33.0	--	--	13 <u>M</u> HNO ₃ -0.04 <u>M</u> HF- 0.1 <u>M</u> Al(NO ₃) ₃	100	100
Alumina-coated UO ₂	8.0	--	--	--	10 <u>M</u> HNO ₃	9.9	--
Uncoated UC ₂	3.7	--	--	0.1	10 <u>M</u> HNO ₃	99.8	--
Uncoated UC ₂	0.7	--	--	0.4	10 <u>M</u> HNO ₃	98.0	--
Uncoated UO ₂	7.0	--	2.0	--	10 <u>M</u> HNO ₃	99.6	--
Uncoated UO ₂	6.8	--	20.3	--	10 <u>M</u> HNO ₃	97.8	--

This technique may also be applicable to fuels containing BeO-coated particles using dissolution techniques developed for sintered BeO.¹⁹ Fuel elements containing alumina-coated particles present a nearly impossible situation because of the inertness of sintered alumina. The graphite matrix burns readily, but the coated particles are virtually unaffected by the combustion. Fuels that are coated with materials such as SiC or that contain impurities such as iron yield combustion residues from which quantitative leaching of the uranium and thorium is difficult. For example, the ash from a graphite-base fuel sphere coated with siliconized SiC retained 2% of the uranium in insoluble form when leached with boiling 10 M HNO₃.

The combustion-dissolution process is not without its shortcomings, however. Because of the high temperatures involved the choice of materials for burner construction is limited, and CO, which can form explosive mixtures with oxygen, is formed in preference to CO₂ unless an excess of oxygen is present. Methods for safely disposing of the radioactive off-gas will have to be developed. In addition, the ash from thorium-bearing fuels can be dissolved only in nitric acid containing small amounts of fluoride ion, a somewhat corrosive solution. Because of the markedly different thermal and environmental conditions imposed in the two steps of the process, it is quite unlikely that a single vessel can be used for the combustion and dissolution.

Low-temperature combustion may alleviate many of these problems. Preliminary work in this area has indicated that the ignition temperature can be lowered several hundred Centigrade degrees by the use of catalysts such as manganese, copper, or lead. For example, United Carbon Products spectroscopic-grade graphite does not ignite below 720°C in a stream of pure oxygen; however, the ignition temperature can be reduced to about 345°C by presoaking the graphite in 0.07 M lead acetate solution, as shown in Table 9. Furthermore, combustion is catalyzed well below the ignition temperature. Untreated graphite showed at most a 0.4% weight loss when exposed for 3 hr to a stream of oxygen at 460°C, but a piece

¹⁹K. S. Warren, L. M. Ferris, and A. H. Kibbey, Dissolution of BeO- and Al₂O₃-Base Reactor Fuel Elements. Part I, ORNL-3220 (Jan. 30, 1962).

of graphite that had been soaked for 3 min in 0.25 M KMnO_4 solution lost 34% of its weight under the same conditions. Further work with such catalysts is in progress.

Table 9. Catalysis of the Combustion of United Carbon Products Graphite (Ultrapurity, spectroscopic grade from Lot 5387; density, 1.55 g/cm^3)

Catalyst ^a	Ignition Temperature (°C)	Combustion Temperature (°C)	Time (hr)	Weight Loss (%)
None	720	311	3	0.00
		334	3	0.00
		459	3	0.37
		459	3	0.05
		471	3	0.23
0.07 <u>M</u> Lead Acetate	345	311	3	3.2
		334	3	6.0
0.25 <u>M</u> KMnO_4	482	448	3	33.6
		459	3	34.4
3.15 <u>M</u> $\text{Cu}(\text{NO}_3)_2$	482	459	3	13.5
		471	3	11.9

^aEach specimen soaked for 3 min in the indicated solution.

90% HNO_3 PROCESS

Graphite matrices are readily disintegrated in 90% HNO_3 (21.5 M) at temperatures from 25°C to the boiling point, about 93°C. Unfortunately, only the matrix is affected; both pyrolytic-carbon- and alumina-coated particles are unaffected. For example, the results presented in Table 10 show that when specimens containing coated particles were disintegrated

to powder (mean particle size about 700 μ) in boiling 90% HNO₃, less than 7% of the uranium and thorium was solubilized. This technique, therefore, does not appear applicable to the processing of graphite-base fuels containing coated particles.

Table 10. Uranium and Thorium Recovery from Fueled Graphite by the 90% HNO₃ Process

(Fuel disintegrated and leached twice for 4 hr with boiling 21.5 M HNO₃)

Fuel	Fuel Composition (wt %)		Recoveries (wt %)	
	Uranium	Thorium	Uranium	Thorium
Uncoated UC ₂	3.0	--	99.4	--
Uncoated UC ₂	15.2	--	99.9	--
Uncoated UC ₂ -ThC ₂	1.3	15.0	99.9	99.8
Pyrolytic-carbon-coated UC ₂ -ThC ₂	9.7	33.5	6.5	4.6
Alumina-coated UO ₂	8.0	--	0.8	--

The technique was studied briefly, however, as a destructive method for evaluating the integrity of coated fuel particles. A similar technique based on electrolytic disintegration has been used at Battelle Memorial Institute.²⁰ The amount of uranium (and/or thorium) dissolved during the acid treatment would be proportional to the number of particle coatings which were defective (or which were susceptible to oxidation). Commercial grades of graphite generally are oxidized very slowly in concentrated nitric acid. Studies with type GBF graphite showed that digestion of powdered samples for periods of up to 100 hr resulted in oxidation of less than 2% of the carbon. Amorphous carbons, however, are oxidized at a much higher rate. Therefore, pyrolytic-carbon coatings that are not highly graphitized may be oxidized.

²⁰R. A. Ewing, T. S. Elleman, and R. B. Price, Trans. Am. Nuclear Soc. 4(1), 152 (1961).

Two batches of pyrolytic-carbon-coated uranium carbide particles were tested using the 90% HNO₃ technique, with results as shown in Table 11. In two 6-hr leaches with boiling acid less than 2% of the uranium was dissolved from batch 3M-D; on the other hand about 48% of the uranium was dissolved from batch NCC-J. Since the weight losses were about those expected from the amounts of uranium dissolved, it is concluded that these results reflect the degree to which the particle coatings were defective. The ultimate usefulness of this technique will be determined only after more intensive study.

Table 11. Evaluation of Pyrolytic-Carbon Coatings on Uranium Carbide Particles Using 90% HNO₃

(Each sample leached twice for 6 hr with boiling 21.5 M HNO₃)

Type of Particles	Uranium Content of Sample (wt %)	Uranium Solubilized (wt %)		Weight Loss (%)	
		First Leach	Second Leach	Calculated	Observed
3M-D	69.24	0.34	2.5	1.9	0
3M-D	68.58	0.33	1.0	0.9	0
NCC-J	44.00	11.8	35.8	21	16.9
NCC-J	43.86	11.5	36.4	21	17.2

ANODIC DISINTEGRATION

Electrolytic disintegration in hot (93°C) 15.8 M HNO₃ did not result in satisfactory recovery of uranium from fueled-graphite specimens containing pyrolytic-carbon-coated uranium carbide fuel particles. The graphite matrix was readily disintegrated, but the particle coatings were not markedly affected; as expected, less than 2% of the uranium was found in solution. Similar results were obtained on unsupported pyrolytic-carbon-coated particles²¹ and at Battelle Memorial Institute with fuels containing alumina-coated UO₂ particles.²⁰

²¹A. H. Kibbey and L. M. Ferris, U-Th Recovery from Pyrolytic-Carbon Coated Carbide Fuel Particles by Electrolysis in Nitric Acid, ORNL-TM-384 (Sept. 26, 1962).

CHLORIDE VOLATILITY PROCESS

Very little work has been done on chloride volatility processing of coated-particle fuels. Two variations are being studied. In the first, uranium would be converted to a volatile chloride using one of several reagents such as CCl_4 , Cl_2 , or COCl_2 and sublimed away from the graphite matrix (graphite reacts only very slowly with chlorinating agents even at relatively high temperatures). The recovered uranium chloride would either be fluorinated to UF_6 or dissolved in an aqueous solution preparatory to solvent extraction. Chlorination techniques are also applicable to the recovery of uranium from combustion ashes.

SUMMARY AND CONCLUSIONS

At this stage of development, combustion-dissolution must be considered the best method for processing graphite-base coated-particle fuels. The chief foreseeable problems with this technique are the treatment of large volumes of radioactive off-gas from the burning step and the probable need for transferring the solid combustion ash to a suitable metallic vessel for the acidic dissolution. In addition, it is doubtful that a single vessel can be utilized for both burning and HNO_3 - HF dissolution because of the corrosiveness of the acidic reagents in the high-nickel-content alloys required to withstand the oxidation conditions.

The alternative method, that of grinding followed by acid leaching, is plagued with potential engineering problems. Grinding is a formidable operation, and even if it could be conducted efficiently the resulting powder would be so fine that its separation from the acidic leach liquor would be extremely difficult by either centrifugation or filtration. The "chemical grinding" methods, 90% HNO_3 and electrolytic disintegration, are inapplicable to the processing of coated-particle fuels, but have found application in the evaluation of as-received and irradiated coated particles.

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